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SYNTHESIS OF AMINO ACIDS FROM SUBSTITUTED CYANOACETIC ESTERS[1]

BY PAUL E. GAGNON AND JEAN L. BOIVIN[2]

Abstract

Nine α-amino acids, namely, *dl*-alanine, *dl*-α-aminobutyric acid, *dl*-α-aminoenanthic acid, *dl*-α-amino-γ-phenoxybutyric acid, *dl*-C-phenylglycine, *dl*-proline, *dl*-ornithine, *dl*-lysine and 2-aminoindane-2-carboxylic acid have been prepared from α-substituted cyanoacetic esters. Pyrrolidine or piperidine was isolated when it was attempted to prepare ornithine or lysine by hydrolysis of diurethanes with hydrochloric acid. When a mixture of formic and hydrochloric acids and water was used as hydrolyzing agent, ornithine or lysine was obtained in low yield in addition to traces of pyrrolidine or piperidine. The following compounds, as far as the authors are aware, have been prepared for the first time: α-cyanopropionhydrazide, benzal α-cyanopropionhydrazide, α-cyanopropionic azide, α-carbethoxyaminopropiononitrile, α-cyanobutyrhydrazide, benzal α-cyanobutyrhydrazide, α-cyanobutyric azide, α-carbethoxyaminobutyronitrile, ethyl α-cyanoenanthate, α-cyanoenanthic hydrazide, benzal α-cyanoenanthic hydrazide, α-cyanoenanthic azide, α-carbethoxyaminoenanthonitrile, 5-(*n*-amyl)-hydantoin, ethyl α-cyano-γ-phenoxybutyrate, ethyl *bis*-β-phenoxyethylmalonate mononitrile, α-cyano-γ-phenoxybutyrhydrazide, benzal α-cyano-γ-phenoxybutyrhydrazide, α-cyano-γ-phenoxybutyric azide, α-carbethoxyamino-γ-phenoxybutyronitrile, 5-(β-phenoxyethyl)-hydantoin, α-cyano-α-phenylacethydrazide, benzal α-cyano-α-phenylacethydrazide, α-cyano-α-phenylacetic azide, ethyl δ-bromo-α-cyanovalerate, δ-bromo-α-cyanovalerhydrazide, benzal δ-bromo-α-cyanovalerhydrazide, δ-bromo-α-cyanovaleric azide, δ-bromo-α-carbethoxyaminovaleronitrile, dibenzal α-cyanoadipic dihydrazide, α-cyanoadipic diazide, α,δ-dicarbethoxyaminoadiponitrile, dibenzal α-cyanopimelic dihydrazide, α-cyanopimelic diazide, α,ϵ-dicarbethoxyaminocapronitrile, 2-cyano-2-carbethoxyindane, 2-cyano-2-carboxylindane hydrazide, benzal 2-cyano-2-carboxylindane hydrazide, 2-cyano-2-carboxylindane azide, 2-cyano-2-carbethoxyaminoindane, 2-aminoindane-2-carboxylic acid, 2-aminoindane-2-carboxylic acid hydrochloride.

Introduction

The Curtius degradation, which permits the replacement of a carbethoxy group by an amino group, was first applied to cyanoacetic ester in 1915 by Darapsky and Hillers, who prepared glycine (3). Later, in 1936, Darapsky (2, pp. 257–267) synthesized α-amino-*n*-valeric acid, α-aminoisoamylacetic acid, and *dl*-leucine from the corresponding alkylcyanoacetic esters. In 1944, Gagnon, Gaudry, and King (4) obtained α-amino-δ-phenoxyvaleric acid, *dl*-methyltyrosine, *dl*-phenylalanine, *dl*-valine and, in 1947, Gagnon, Savard, Gaudry, and Richardson (5) prepared *dl*-norleucine, *dl*-isoleucine, *dl*-S-benzylhomocysteine and *dl*-methionine by the same method.

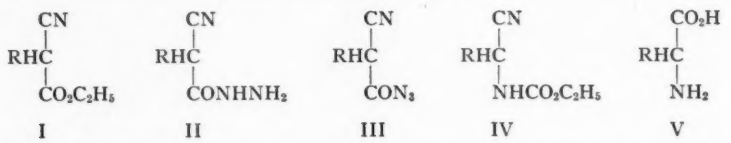
[1] *Manuscript received March 11, 1948.*

Contribution from the Department of Chemistry, Laval University, Quebec. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfilment of the requirements for the degree of Doctor of Science.

[2] *Holder of a Shawinigan Chemicals Limited Research Scholarship, and later of a Bursary under the National Research Council of Canada.*

The present investigations were undertaken primarily to extend the Darapsky method to the syntheses of a cyclic amino acid, proline, diamino acids, ornithine and lysine, and a disubstituted amino acid, 2-aminoindane-2-carboxylic acid. Experience was gained by first preparing: alanine (V, R = methyl); α-aminobutyric acid (V, R = ethyl); α-aminoenanthic acid (V, R = *n*-amyl); α-amino-γ-phenoxybutyric acid (V, R = β-phenoxyethyl), and C-phenylglycine (V, R = phenyl).

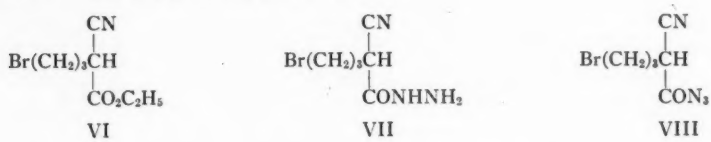
The starting materials, the substituted cyanoacetates, were prepared by three different methods, The first one, often used in these investigations, was the alkylation of ethyl cyanoacetate by alkyl halides in the presence of sodium ethylate. The yields varied from 45 to 80%.



I II III IV V

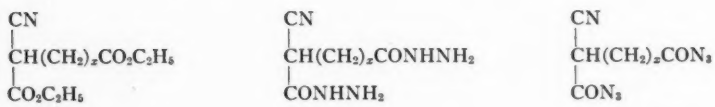
R = methyl (CH_3—); ethyl (CH_3CH_2—); *n*-amyl ($CH_3CH_2CH_2CH_2CH_2$—); β-phenoxyethyl ($C_6H_5O(CH_2)_2$—); phenyl (C_6H_5—).

RH must be replaced by R_2 in the formulae I, II, III, IV, and V for the disubstituted compounds. R_2 = *o*-xylylene ($C_6H_4 : (CH_2)_2$=).



VI VII VIII

IX X



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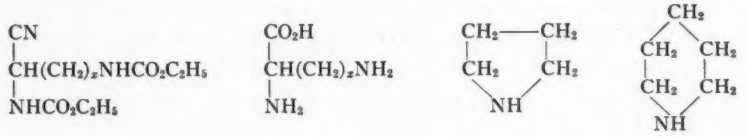

XIV XV XVI XVII

Ornithine, $x = 3$. Lysine, $x = 4$.

The second method used was the carbethoxylation of a nitrile in the α-position by ethyl carbonate in the presence of sodium ethylate and elimination of the alcohol produced in the reaction (10).

$$C_6H_5CH_2CN + CO(OC_2H_5)_2 + NaOC_2H_5 \longrightarrow C_6H_5\underset{\displaystyle CO_2C_2H_5}{\underset{|}{C}}NaCN + 2EtOH$$

$$C_6H_5\underset{\displaystyle CO_2C_2H_5}{\underset{|}{C}}NaCN + HCl \longrightarrow C_6H_5\underset{\displaystyle CO_2C_2H_5}{\underset{|}{C}}HCN + NaCl$$

The third and best method consists of simultaneously condensing aldehydes or ketones with ethyl cyanoacetate and hydrogenating the intermediate product in the presence of palladinized charcoal (1).

The formation of the hydrazides (II) from the starting materials took place quantitatively at room temperature simply by mixing the esters (I) with hydrazine hydrate; the reaction proceeded rapidly with evolution of heat. Most of the hydrazides obtained were crystalline, except α-cyanopropionhydrazide (II, R = methyl), which was a viscous liquid. An attempt to obtain it in the crystalline state resulted in the formation of a pyrazolone (8). All the hydrazides were identified by their condensation products with benzaldehyde. The hydrazides were transformed into the corresponding azides (III) by treatment with nitrous acid, the azides being extracted with ether. The urethanes were prepared by boiling the alcoholic solutions of the azides under reflux for about half an hour. The urethanes were all viscous brown liquids, except α-phenyl-α-carbethoxyaminoacetonitrile (IV, R = phenyl), which was a crystalline solid already described (9).

The hydrolysis of the urethanes with hydrochloric acid required in some cases long periods of heating when the urethanes were slightly soluble; the yields were low. In these cases, a mixture of equal portions by volume of commercial formic acid, concentrated hydrochloric acid, and water was used with advantage. The mixture usually dissolved the urethanes; the period of heating was decreased from 48 to one hour and the yields of amino acids were much higher.

The formic – hydrochloric acid mixture was found to be advantageous for the formation of amino acids having an aliphatic chain in the α-position; the yields were good and the period of heating short. Yields decreased with increasing length of the aliphatic chain. For amino acids that have an aromatic ring in the lateral chain, low yields were obtained; hydrochloric acid (20%) was better; for instance, the yield of C-phenylglycine increased from 20 to 50%.

The amino acids, alanine, α-aminobutyric acid, α-aminoenanthic acid, α-amino-γ-phenoxybutyric acid, C-phenylglycine and 2-aminoindane-2-carboxylic acid were easily obtained.

The starting material (VI) for proline (X) was prepared by condensing trimethylene bromide with cyanoacetic ester. The amino acid was obtained by simultaneous hydrolysis and cyclization of the urethane (IX, R = γ-bromopropyl). It was isolated as its copper salt. Although the yield of proline was low, this synthesis proved that the Darapsky method could be applied to an ester (VI) containing a bromine atom in the lateral chain.

The failure of experiments to extend the method to the synthesis of the diamino acids, ornithine (XV, $x = 3$) and lysine (XV, $x = 4$) from diethyl α-cyanoadipate (XI, $x = 3$) and diethyl α-cyanopimelate (XI, $x = 4$) has been reported in the literature (4). In the present work, similar results were obtained when hydrochloric acid (20%) was used to hydrolyze the corresponding urethanes (XIV). Pyrrolidine (XVI) and piperidine (XVII) were formed and no amino acid was obtained. However, when the formic – hydrochloric acid mixture was used, ornithine and lysine were obtained in addition to traces of pyrrolidine and piperidine. Long periods of hydrolysis lowered the yields of amino acids and favored the formation of pyrrolidine.

This result clearly indicates that the Darapsky method is of wider application than it was previously thought to be.

Experimental*

Substituted Cyanoacetates (I)

The ethyl α-substituted cyanoacetates, $RCH(CN)COOC_2H_5$, were prepared by four different methods.

(*a*) *I, R = n-Amyl* (C_5H_{11}—); *β-Phenoxyethyl* ($C_6H_5O(CH_2)_2$—); *γ-Carbethoxypropyl* ($EtO_2C(CH_2)_3$—); *δ-Carbethoxybutyl* ($EtO_2C(CH_2)_4$—)

To a solution of sodium ethoxide (0.5 mole of sodium and 250 ml. of absolute ethyl alcohol), ethyl cyanoacetate (1.0 mole) was added. The mixture was cooled with running water and a solution of alkyl halide (0.5 mole) in dry ethanol was added slowly. The suspension was boiled under reflux on a water bath until the medium was neutral to wet litmus paper. The alcohol was removed by distillation and the residual sludge poured into cold water. The oily layer formed was separated and the aqueous layer, made faintly acid to litmus paper, extracted several times with ether. The oily layer and the ethereal solutions were dried over anhydrous sodium sulphate and the ether evaporated. The residue was fractionated under reduced pressure.

(*b*) *I, R = Methyl* (CH_3—); *Ethyl* (C_2H_5—)

To a solution of sodium ethoxide (0.5 mole of sodium and 250 ml. of absolute ethyl alcohol), ethyl cyanoacetate (1.0 mole) was added. The mixture was evaporated to dryness under reduced pressure and the residue heated in an oil bath maintained at 125° C. The residue was disintegrated and ether (200 ml.) was added. To the suspension cooled under running water a solution of

* *All melting points are uncorrected.*

methyl or ethyl iodide (0.5 mole) in dry ether (200 ml.) was added dropwise. The mixture was refluxed for half an hour, when it was neutral to wet litmus paper, and worked out as above mentioned.

(*c*) *I, R = Bromopropyl* ($Br(CH_2)_3$—)

To an ice cold solution of sodium ethoxide (0.5 mole of sodium and 200 ml. of absolute ethyl alcohol), a mixture of ethyl cyanoacetate (0.5 mole) and trimethylene bromide (0.5 mole) was added drop by drop. The suspension was allowed to stand at room temperature for one day. It was poured into cold water and the mixture extracted with ether. The ethereal solution was worked out in the usual way.

(*d*) *I, R = o-Xylylene* ($C_6H_4 : (CH_2)_2$=)

To a warm solution of sodium ethoxide (0.5 mole of sodium and 200 ml. of absolute ethyl alcohol), dry ether was added. Ethyl cyanoacetate (56.5 gm., 0.5 mole), dissolved in dry ether (150 ml.), and *o*-xylylene dibromide (66 gm., 0.25 mole), dissolved in dry ether (250 ml.), were rapidly poured into the mixture, which was allowed to stand one hour at room temperature. The suspension was refluxed for two hours on the water bath to complete the reaction, cooled, poured into cold water (500 ml.), and the ether was decanted. The ethereal solution was worked out as above.

The properties and yields of the substituted cyanoacetates are given in Table I.

TABLE I

ETHYL α-SUBSTITUTED CYANOACETATES, $RCH(CN)COOC_2H_5$

R	Starting material	Yield, %	B.p., °C.	Formula	Nitrogen, %		n_D^{25}
					Calc.	Found	
Methyl*	CH_3I	80	87– 88 (15 mm.)	$C_6H_9O_2N$	11.0	11.0	1.4110
Ethyl**	C_2H_5I	89	94– 95 (15 mm.)	$C_7H_{11}O_2N$	9.93	9.89	1.4163
n-Amyl	$CH_3(CH_2)_4Br$	82	99–101 (3 mm.)	$C_{10}H_{17}O_2N$	7.65	7.65	1.4270
β-Phenoxyethyl	$C_6H_5O(CH_2)_2Br$	62	210–220 (15 mm.)	$C_{13}H_{15}O_3N$	6.06	5.89	1.5032
bis-β-phenoxyethyl†	$C_6H_5O(CH_2)_2Br$	32	270–274 (15 mm.)	$C_{21}H_{25}O_4N$	3.96	4.03	—
Phenyl††	$C_6H_5CH_2CN$	85	141–142 (6 mm.)	—	—	—	1.5017
γ-Bromopropyl	$Br(CH_2)_3Br$	18	125–126 (3 mm.)	$C_8H_{12}O_2NBr$‡	5.98	5.95	1.4280
γ-Carbethoxypropyl‡‡	$EtO_2C(CH_2)_3Br$	62	178–186 (13 mm.)	—	—	—	1.4425
δ-Carbethoxybutyl‡‡	$EtO_2C(CH_2)_4I$	85	160–162 (2 mm.)	—	—	—	1.4150
o-Xylylene§	$C_6H_4 : (CH_2Br)_2$	95	169–170 (18 mm.)	$C_{12}H_{13}O_2N$	6.51	6.55	—

* *Ref.* (7) ** *Ref.* (*1, 6*). † *M.p. 60° to 61° C.* †† *Ref.* (*10*).
‡ *Calc. Br, 34.2%. Found: Br, 33.8%.* ‡‡ *Ref.* (*4*). § *M.p. 53° to 54° C.*

Substituted Cyanoacethydrazides (II)

The substituted cyanoacetates (0.1 mole) were stirred with hydrazine hydrate (100%, 5.0 gm., 0.1 mole). The reactions were exothermic. The solutions were allowed to stand at room temperature, preferably in an evacuated desiccator over phosphorus pentoxide to absorb the alcohol formed. All

the hydrazides prepared crystallized quantitatively except α-cyanopropionhydrazide, which remained a viscous liquid; an attempt to crystallize this material resulted in the formation of a pyrazolone.

Dihydrazides of Cyanopimelic or Cyanoadipic Acid (XII)

Diethyl α-cyanoadipate or diethyl α-cyanopimelate (0.05 mole) was stirred with hydrazine hydrate (100%, 0.1 mole). The reactions were slightly exothermic. The solutions were placed in an evacuated desiccator over phosphorus pentoxide where complete solidification occurred after two days. The products were recrystallized from a large volume of ethanol from which they separated incompletely. A ferric chloride test for the presence of the pyrazolone ring seemed to be positive, but this was due to the basic properties of the dihydrazides.

2-Cyano-2-carboxylindane Hydrazide

2-Cyano-2-carbethoxyindane (4.4 gm., 0.02 mole) was dissolved in ethanol (95%, 20 ml.). The solution was stirred with hydrazine hydrate (100%, 0.95 gm., 0.019 mole) and left at room temperature for two days. A solid crystallized out.

The properties of the hydrazides are given in Table II.

TABLE II

α-SUBSTITUTED CYANOACETHYDRAZIDES, $RCH(CN)CONHNH_2$

R	M.p., °C.	Formula	Nitrogen, %	
			Calc.	Found
Ethyl	95–96	$C_5H_9ON_3$	33.0	32.8
n-Amyl	61–62	$C_8H_{15}ON_3$	24.8	24.7
Phenoxyethyl	99–100	$C_{11}H_{13}O_2N_3$	19.6	19.5
Phenyl	110–111	$C_9H_9ON_3$	24.0	23.8
γ-Bromopropyl	200–201	$C_6H_{10}ON_3Br$*	19.1	18.8
o-Xylylene	222–223	$C_{11}H_{11}ON_3$	20.9	20.8

* *Calc. Br, 36.3%. Found Br. 35.8%.*

The hydrazides were identified by condensation with benzaldehyde in the usual way. The properties of the products obtained are given in Table III.

Amino Acids (V, X, XV)

The substituted cyanoacethydrazides were converted through the azides to the corresponding urethanes in the manner originally outlined by Darapsky (2, pp. 257–267). The crude urethanes were viscous brown liquids, except α-carbethoxyamino-α-phenylacetonitrile, which was crystalline (9). They were hydrolyzed (5) with two different hydrolyzing agents, hydrochloric acid (20%) and a mixture of equal portions by volume of concentrated hydrochloric

TABLE III

BENZAL DERIVATIVES

Compound	M.p., °C.	Formula	Nitrogen, %	
			Calc.	Found
$RCH(CN)CONHN{:}CHC_6H_5$				
R = Methyl	160–161	$C_{11}H_{11}ON_3$	20.9	20.6
Ethyl	167–168	$C_{12}H_{13}ON_3$	19.5	19.4
n-Amyl	150–151	$C_{15}H_{19}ON_3$	16.3	16.0
Phenoxyethyl	154–155	$C_{12}H_{17}O_2N_3$	13.7	13.6
Phenyl	203–204	$C_{16}H_{13}ON_3$	15.9	15.4
γ-Bromopropyl	249–251	$C_{13}H_{14}ON_3Br$*	13.6	13.4
o-Xylylene	292–294	$C_{18}H_{15}ON_3$	14.5	14.0
Dibenzal α-cyanoadipic	200–201	$C_{21}H_{21}O_2N_5$	16.4	16.0
Dibenzal α-cyanopimelic dihydrazide	214–215	$C_{22}H_{23}O_2N_5$	15.8	15.2

* *Calc. Br, 25.9%. Found: Br, 25.2%.*

acid, formic acid (85%), and water. The amino acids were isolated by adjusting the solutions to the isoelectric point or by the lead oxide method. 2-Aminoindane-2-carboxylic acid was isolated at its isoelectric point.

The diamino acid ornithine was prepared by a different method. The corresponding diurethane treated with hydrochloric acid (20%) yielded pyrrolidine and not the amino acid.

The diurethane (10 gm.) was treated with hydrochloric acid (20%, 100 ml.) and the mixture refluxed for 48 hr. The solution was evaporated to dryness under reduced pressure. Half of the residue was dissolved in water, and the solution was made strongly alkaline with sodium hydroxide and extracted with ether in a continuous extractor. Evaporation of the ethereal solutions yielded a small quantity of pyrrolidine. The other portion of the residue was dissolved in water and the solution boiled with lead oxide until free from basic volatile constituents. The mixture was filtered hot, treated with hydrogen sulphide to remove lead, and boiled for some time. The solution showed a negative ninhydrin test. No amino acid was present in the solution.

However, the diurethane gave rise to ornithine in addition to traces of pyrrolidine with the other hydrolyzing medium.

The crude diurethane was hydrolyzed with a mixture of commercial formic acid (20 ml.), concentrated hydrochloric acid (20 ml.), and water (20. ml.) for two hours in an oil bath maintained at 135° C. The solution was evaporated to dryness under reduced pressure. The residue was dissolved in water and the solution boiled with lead oxide. Some pyrrolidine evaporated. The mixture was filtered hot, treated with hydrogen sulphide to remove lead, and boiled for some time. The solution showed a positive ninhydrin test. Sulphuric acid was added and the solution evaporated to dryness. Ornithine was isolated as ornithine sulphate and identified through its dipicrate.

For lysine similar results were obtained. Instead of pyrrolidine, piperidine only was formed when hydrochloric acid (20%) was used. Lysine and traces of piperidine were formed when the diurethane was subjected to hydrolysis for three hours in the formic – hydrochloric acid mixture. Lysine was isolated as its dihydrochloride.

The properties and yields of the amino acids obtained are listed in Table IV, together with the properties of the derivatives prepared.

TABLE IV

AMINO ACIDS OBTAINED BY HYDROLYSIS OF CORRESPONDING URETHANES

Compound	Hydrolyzing agent	Time, hr.	Yield, %	Formula	Nitrogen, %		Derivative
					Calc.	Found	
dl-Alanine	Mixed acids	1	70	$C_3H_7O_2N$	15.7	15.8	Hydantoin, m.p., 145–146° C.
dl-α-aminobutyric acid	Mixed acids	2	69	$C_4H_9O_2N$	—	—	Hydantoin, m.p. 119–120° C.
dl-α-aminoenanthic acid	Mixed acids	6	55	$C_7H_{15}O_2N$	9.65	9.65	Hydantoin, m.p. 142–143° C.*
dl-α-amino-γ-phenoxy-butyric acid	20% HCl	48	51	$C_{10}H_{13}O_3N$	7.18	7.02	Hydantoin, m.p. 156–158° C.**
dl-C-phenylglycine	20% HCl	48	50	$C_8H_9O_2N$	—	—	Hydantoin, m.p. 177–178° C.
dl-proline	Mixed acids	5	16	$C_5H_9O_2N$	12.1	11.6	Copper salt.†
dl-ornithine	Mixed acids	2	23	$C_5H_{12}O_2N_2 \cdot H_2SO_4$	15.4	15.2	Dipicrate, m.p. 195–200° C.††
dl-lysine	Mixed acids	3	22	$C_6H_{14}O_2N_2 \cdot 2HCl$	12.8	12.0	Dipicrate, m.p. 188–190° C. ‡
2-Aminoindane-2-carboxylic acid	Mixed acids	4	35	$C_{10}H_{11}O_2N$	7.96	7.88	Hydrochloride ‡‡

* *Calc. for* $C_8H_{14}O_2N_2$ *: N, 16.5. Found: N, 16.6%.*
** *Calc. for* $C_{11}H_{12}O_3N_2$ *: N, 12.7%. Found: N, 13.0%.*
† *Calc. for* $(C_5H_8O_2N)_2Cu$*: N, 4.81%. Found: N, 4.68%.*
†† *Calc. for* $C_5H_{12}O_2N_2$ *:* $2C_6H_3O_7N_3$ *: N, 19.0%. Found: N, 19.4%.*
‡ *Calc. for* $C_6H_{14}O_2N_2$ *:* $2C_6H_3O_7N_3$ *: N, 18.5%. Found: N, 18.6%.*
‡‡ *Calc. for* $C_{10}H_{11}O_2N \cdot HCl$ *: N, 6.54%. Found: N, 6.51%.*

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THE SYNTHESIS AND BIOLOGICAL TOXICITIES OF SOME DDT HOMOLOGUES AND RELATED COMPOUNDS[1]

By G. T. Barry[2] and R. Boyer

Abstract

The compounds 1-(methoxy)-1-(4-chlorophenyl)-2,2,2-trichloroethane, 1-(ethoxy)-1-(4-chlorophenyl)-2,2,2-trichloroethane, 1-(trichloroacetoxy)-1-(4-chlorophenyl)-2,2,2-trichloroethane, and 1-(4-chlorophenyl)-2,2,2-trichloroethyl methyl succinate have been prepared for the first time as outlined below. The toxicity of these compounds and several others against *Drosophila melanogaster* (fruit fly) as compared to DDT is also reported. None of the compounds submitted was found to be superior to DDT as a contact insecticide.

Introduction

The well known compound 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane (*p,p'*-DDT) has found extensive application as a contact insecticide especially against lice and mosquitoes. Although DDT and '666' (gamma-hexachlorocyclohexane) are among the most effective contact insecticides known, many homologues of DDT such as 1,1,1-trichloro-2,2-*bis*(4-methoxyphenyl)ethane, 1,1,1-trichloro-2,2-*bis*(4-fluorophenyl)ethane (10) and 1,1,1-trichloro-2,2-*bis*-(4-tolyl)ethane (3) are also toxic to insects.

The preparation of DDT (14) is accomplished by condensing chloral with chlorobenzene using sulphuric acid as catalyst.

$$CCl_3CHO + C_6H_5Cl \xrightarrow{H_2SO_4} \underset{\text{Carbinol}}{CCl_3CH(OH)C_6H_4Cl}$$

$$CCl_3CH(OH)C_6H_4Cl + C_6H_5Cl \xrightarrow{H_2SO_4} \underset{\text{DDT}}{CCl_3CH(C_6H_4Cl)_2} + H_2O$$

Both the ortho and para carbinols, 1-(2-chlorophenyl)-2,2,2-trichloroethanol and 1-(4-chlorophenyl)-2,2,2-trichloroethanol, can be isolated as intermediates in about 5% total yield from the above reaction (7). The preparation of some of the following DDT homologues was performed by using the para carbinol intermediate as the starting material.

1-(4-Chlorophenyl)-2,2,2-trichloroethanol was obtained by chlorinating 1-(4-chlorophenyl)ethanone (8, p. 396) to 1-(4-chlorophenyl)-2,2,2-trichloroethanone and reducing the latter to the carbinol with aluminum isopropoxide (1, pp. 198–203). Both the acetate and propionate derivatives of 1-(4-chlorophenyl)-2,2,2-trichloroethanol were prepared by heating with the respective acid anhydrides (9). The butyrate was formed by heating the carbinol with butyryl chloride (9) and 1-(trichloroacetoxy)-1-(4-chlorophenyl)-2,2,2-trichloroethane from the carbinol and trichloroacetyl chloride.

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Contribution from the Organic Chemistry Laboratory, McGill University, Montreal, Que.

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The methoxy and ethoxy derivatives, 1-(methoxy)-1-(4-chlorophenyl)-2,2,2-trichloroethane and 1-(ethoxy)-1-(4-chlorophenyl)-2,2,2-trichloroethane, were prepared by heating the carbinol under reflux with silver oxide and methyl or ethyl iodide.

The formation of 1-(4-chlorophenyl)-2,2,2-trichloroethyl methyl succinate was accomplished by preparing monomethyl succinate from succinic anhydride and methanol (2), and converting the mono ester to monomethyl succinyl chloride (13) with thionyl chloride. Upon heating the carbinol with monomethyl succinyl chloride, the 1-(4-chlorophenyl)-2,2,2-trichloroethyl methyl succinate derivative was readily obtained.

In the attempt to prepare 1-(4-trichloromethylphenyl)-2,2,2-trichloroethanol by reduction of 1-(4-trichloromethylphenyl)-2,2,2-trichloroethanone with aluminum isopropoxide, a compound with an empirical formula $C_{12}H_{13}O_3Cl_3$ was isolated. The structure of the compound is not certain, but it is believed to be 4-(1-hydroxy-2,2,2-trichloroethyl)isopropyl benzoate. Both 1,1-*bis*(4-chlorophenyl)ethylene and 1-(4-chlorophenyl)-1-(2-chlorophenyl)ethylene were prepared from 1,1,1-trichloroethane and chlorobenzene using aluminum chloride as condensing agent. These, and several homologous compounds were tested against *Drosophila melanogaster* (fruit fly). For comparative purposes the relative toxicities of these compounds, compared to DDT as unity, are indicated in Table I.

TABLE I

TOXICITY OF SEVERAL HOMOLOGUES OF DDT AGAINST *Drosophila melanogaster*

No.	Name of compound	Formula	Activity, assuming DDT as unity
I	1-(4-chlorophenyl)-1-(acetoxy)-2,2,2-trichloroethane	$CCl_3CH(C_6H_4Cl)$ $\vert$ $OCOCH_3$	1/10
II	1-(4-trichloromethylphenyl)-2,2,2-trichloroethanone	$CCl_3C_6H_4COCCl_3$	1/50
III	1-(4-chlorophenyl)-2,2,2-trichloroethanol	$CCl_3CH(OH)C_6H_4Cl$	1/50
IV	1-(4-chlorophenyl)-1-(2-chlorophenyl)ethylene	$(p\text{-}ClC_6H_4)(o\text{-}ClC_6H_4)C : CH_2$	1/50
V	1-(4-chlorophenyl)-1-(methoxy)-2,2,2-trichloroethane	$ClC_6H_4CH(OCH_3)CCl_3$	1/75
VI	1-(4-chlorophenyl)-1-(ethoxy)-2,2,2-trichloroethane	$ClC_6H_4CH(OC_2H_5)CCl_3$	1/75
VII	1,1-*bis*(4-chlorophenyl)ethylene	$(ClC_6H_4)_2C : CH_2$	1/100
VIII	1-(4-chlorophenyl)-2,2,2-trichloroethanone	$ClC_6H_4COCCl_3$	1/250

The following compounds exhibited either no activity or only slight activity of the order of 1/500th the toxicity of DDT: 1-(4-chlorophenyl)-2,2-dichloroethanone (IX), 4-bromophenylsulphonic acid (X), 1,1,1,2-tetrachloroethylbutyl ether (XI), 1-(4-chlorophenyl)-2,2,2-trichloroethylpropionate (XII), 1-(4-chlorophenyl)-2,2,2-trichloroethylbutyrate (XIII), 1-(4-chlorophenyl)-1-trichloroacetoxy-2,2,2,-trichloroethane (XIV), and chloralid (XV). No insecticidal activity was shown by the following compounds at any concentration: pentachloroethane (XVI), *bis*(2-chlorophenyl)acetic acid (XVII), 4,4′-dichlorobenzil (XVIII), chloralbutyl alcoholate (XIX), 1-(4-chlorophenyl)-2,2,2-trichloroethyl methyl succinate (XX), 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane (XXI), 1,1-*bis*(4-chlorophenyl)-2,2-dichloroethylene (XXII), chloral hydrate (XXIII), 4,4′-dichlorobenzophenone (XXIV), 2,4-dichlorobenzophenone (XXV), 4-methylacetophenone (XXVI), 4,4′-dibromophenylsulphone (XXVII), and $C_{12}H_{13}O_3Cl_3$ (XXVIII).

Discussion

From Table I it is noted that ketones II and VIII have reactivities of 1/50th and 1/250th of that of DDT. The activity of the latter was augmented five times upon reduction of the carbonyl group to give compound III. If any correlation exists in the activities of these ketones and their corresponding carbinols, then the reduction of the carbonyl group in II should give a highly active compound. The greater activity of compound II compared to VIII arises from the substitution of a trichloromethyl group (CCl_3) for a chlorine(Cl) in the para position of the benzene ring. The above observations indicate that the chlorinated methyl and polymethyl benzenes and chlorinated (polymethylphenyl) trichloroethanones should be further investigated as possible contact insecticides.

There has been a great deal of controversy over the mechanism by which DDT acts as an insecticide. Neither the mechanism proposed by Läuger and co-workers (11) nor those advanced by Martin and Wain (12) or by Fleck and Haller (6) appear to be unequivocally supported by the compounds tested in this laboratory.

In summary, none of the 28 compounds tested were found to be superior to DDT as a contact insecticide. The experimental data suggest no theory concerning the essential physical or chemical properties required for the extreme toxicity of DDT.

Experimental

1. *1-(4-Chlorophenyl)-2,2,2-trichloroethanol and Derivatives*

The 1-(4-chlorophenyl)-2,2,2-trichloroethanol was prepared by reducing 1-(4-chlorophenyl)-2,2,2-trichloroethanone (8, p. 396) with aluminum isopropoxide (1, pp. 198-203). The oily reduction product was identified as 1-(4-chlorophenyl)-2,2,2-trichloroethanol by conversion to the acetate (9) and

to DDT. The yield was over 90% of the theoretical (based on conversion to the acetate in 91% yield). Upon standing for several days the product crystallized, m.p. 43° C. It was then recrystallized from *n*-heptane, m.p. 47° C.

2. *1-(4-Chlorophenyl)-1-(trichloroacetoxy)-2,2,2-trichloroethane*

Into a 50 cc. round bottomed flask were placed 3.9 gm. (0.015 mole) of 1-(4-chlorophenyl)-2,2,2-trichloroethanol and 5.46 gm. (0.03 mole) of trichloroacetyl chloride. The solution was heated under reflux for 18 hr. at 130° to 150° C., cooled, diluted with 10 cc. of water, and reheated to 60° C. for a few minutes to hydrolyze any unreacted acid chloride. The water layer was decanted and 10 cc. of ether added to the oily residue. The ether solution on cooling in a dry ice – acetone bath, gave needle-shaped crystals, m.p. 67° to 68° C. The product was recrystallized from acetone, m.p. 71° C., and gave a yield of over 80% of the theoretical. Calc. for $C_{10}H_5O_2Cl_7$: Cl, 61.25%. Found: Cl, 61.00, 60.85%.

3. *1-(4-Chlorophenyl)-1-(methoxy)-2,2,2-trichloroethane*

Into a 50 cc. round bottomed flask were placed 3.9 gm. (0.015 mole) of 1-(4-chlorophenyl)-2,2,2-trichloroethanol, 8.6 gm. (0.06 mole) of methyl iodide, and 3 gm. of silver oxide. The reaction was initiated by gently heating the flask under reflux on the steam bath, then controlled by immersing in cold water. An additional 3.9 gm. of silver oxide was added to the flask, making a total of 6.9 gm. (0.03 mole). The flask was heated under reflux for six hours, cooled, and the contents extracted with two separate 20 cc. portions of ether. The combined ether extracts were filtered, poured into a distilling flask, and the ether evaporated by heating. The residue was distilled at 86° to 88° C. under 1 mm. pressure. The distillate crystallized when cooled at −20° C. for several hours, m.p. 28° to 29° C. The yield was 2.7 gm., or 65%. Calc. for $C_9H_8OCl_4$: Cl, 51.79%. Found: Cl, 51.76, 51.66%. Molecular weight in acetone: calc., 274; found, 269, 271.

4. *1-(4-Chlorophenyl)-1-(ethoxy)-2,2,2-trichloroethane*

Into a 50 cc. round bottomed flask were placed 3.9 gm. (0.015 mole) of 1-(4-chlorophenyl)-2,2,2-trichloroethanol, 6.9 gm. (0.03 mole) of silver oxide, and 9.4 gm. (0.06 mole) of ethyl iodide. The flask was heated under reflux for six hours, cooled, extracted with two separate 20 cc. portions of ether, and the combined extracts filtered. The ether was evaporated and the distillate collected at 90° to 94° C. under 0.4 mm. On standing for several days at room temperature, the distillate crystallized and after drying on porous plate melted at 46° to 46.5° C. The product was recrystallized from glacial acetic acid, m.p. 48° C. The material was quite soluble in low boiling petroleum ether, dioxane, nitromethane, methyl and ethyl alcohols, dibutylether, isoamyl alcohol, and benzene. The yield was 37% of the theoretical and the crystals were square-shaped platelets. Calc. for $C_{10}H_{10}OCl_4$: Cl, 49.27%. Found: Cl, 49.02, 49.25%. Molecular weight in acetone: calc., 288; found, 284, 303.

5. *1-(4-Chlorophenyl)-2,2,2-trichloroethyl Methyl Succinate*

Into a 50 cc. round bottomed flask were placed 3.9 gm. (0.015 mole) of 1-(4-chlorophenyl)-2,2,2-trichloroethanol and 3.02 gm. (0.03 mole) of monomethyl succinyl chloride (2, 13). The flask was heated under reflux for 18 hr. at 120° to 140° C., cooled, diluted with 20 cc. of water, and set aside for four hours. The water layer was discarded and the product washed with a fresh 20 cc. portion of water. Ether (20 cc.) was added to the residual oil, and the whole dried over 2 gm. of sodium sulphate. The ether was evaporated, and the distillate, which was collected at 183° to 186° C. under 0.25 mm., was crystallized upon cooling in a dry-ice acetone bath, m.p. 38° to 39° C. The product was dissolved in 4 cc. of 95% ethanol and heated to boiling. A few drops of formamide was added to give incipient cloudiness. After cooling in air and then in the refrigerator for several days, crystals were obtained, m.p. 41° C. The weight was 4.7 gm. or 84% of the theoretical yield. Calc. for $C_{13}H_{12}O_4Cl_4$: Cl, 37.94%. Found: Cl, 37.75, 38.01%. Molecular weight in acetone: calc., 374; found, 372, 369.

6. *Attempted Preparation of 1-(4-Trichloromethylphenyl)-2,2,2-trichloroethanol*

In the attempted reduction of 1-(4-trichloromethylphenyl)-2,2,2-trichloroethanone (5) to 1-(4-trichloromethylphenyl)-2,2,2-trichloroethanol with aluminum isopropoxide, a compound with an empirical formula $C_{12}H_{13}O_3Cl_3$ was obtained.

Into a 500 cc. round bottomed flask were placed 113.7 gm. (0.33 mole) of 1-(4-trichloromethylphenyl)-2,2,2-trichloroethanone, 300 cc. of dry isopropyl alcohol, and 70 gm. (0.34 mole) of aluminum isopropoxide. The solution was heated under reflux distillation as described in Organic Reactions (1, pp. 198-203) until a negative acetone test was obtained from the distillate with 2,4-dinitrophenylhydrazine. The reaction mixture was hydrolyzed with 475 cc. of solution containing 175 cc. of concentrated hydrochloric acid, extracted with three portions of ether, 250, 150, and 100 cc. respectively, and the extracts combined and dried over sodium sulphate. The dried extract was poured into a 250 cc. Claisen flask and the ether distilled. The residue would not distill under reduced pressure because of rapid decomposition. (This was probably decomposition of the ortho ester.) The oily product was transferred to a 500 cc. round bottomed flask, equipped with a side arm at the point where the bulb and neck of the flask joined. With the flask immersed in a sand bath, a yellow, oily distillate was collected with decomposition at 135° to 150° C. under 1 mm. Crystals weighing 24.1 gm. and melting at 88° C. were obtained by rubbing the oil in petroleum ether. A portion of this material was recrystallized several times from petroleum ether, m.p. 95° to 96° C., and was found to give a positive ester test (4). Calc. for $C_{12}H_{13}O_3Cl_3$: C, 46.30; H, 4.17; Cl, 34.18%. Found: C, 46.16, 46.13; H, 4.25, 4.04; Cl, 33.90, 33.78%.

7. *1,1-bis(4-Chlorophenyl)ethylene*

Into a 500 cc. round bottomed, three-necked flask, equipped with a mercury seal stirrer, water cooled reflux condenser, and separatory funnel, were placed 40.5 gm. (0.3 mole) of aluminum chloride and 67.2 gm. (0.6 mole) of chlorobenzene. A solution of 26.7 gm. (0.2 mole) of 1,1,1-trichloroethane dissolved in 22.4 gm. (0.2 mole) of chlorobenzene was added dropwise into the stirred reaction mixture over a 45 min. period. The addition was accompanied by a copious evolution of hydrogen chloride gas. The reaction was initiated at room temperature, cooled to 5° to 10° C. with an ice bath, and the mixture stirred for seven hours after the last addition of 1,1,1-trichloroethane. The product was hydrolyzed by pouring it over an ice and hydrochloric acid mixture and allowing it to stand for three hours. The water–oil solution was separated and the water layer extracted with three separate portions of ether, 75, 50, and 50 cc. respectively. The combined oil and ether extracts were steam distilled. The non-distillable residue was dissolved in 75 cc. of ether and dried over calcium chloride. The dried ether solution was distilled and the product collected at 150° to 160° C. under 11 mm. pressure. The distillate, which weighed 22 gm., partially crystallized upon cooling. The crystals, collected on a filter, weighed 10 gm., m.p. 80° to 81° C. The filtrate oil was set aside for further investigation. After two recrystallizations from ethanol, the melting point rose to 86° C. Further recrystallizations from ethanol or chloroform did not raise the melting point. This was a 20% yield of 1,1-*bis*(4-chlorophenyl)ethylene. Calc. for $C_{14}H_{10}Cl_2$: Cl, 28.45%. Found: Cl, 28.25, 28.20%. Molecular weight in acetone: calc., 249; found, 246, 250, 241.

The uncrystallized oil was redistilled in three fractions: the first fraction was collected up to 137° C. at 5.8 mm. and weighed 0.9 gm.; the second, between 137° and 139° C., weight 3 gm.; the third, between 139° and 142° C., weight approximately 3 gm. The last fraction was slightly colored. The combined weight of distillates was 7 gm. Analysis of No. 2 distillate:— Calc. for $C_{14}H_{10}Cl_2$: Cl, 28.45%. Found: Cl, 28.10, 28.35%. Molecular weight in acetone: calc., 249; found, 251, 258.

The structure of the crystalline and oily products was obtained by oxidation.

Into a 20 cc. beaker were placed 0.2 gm. of the 1,1-*bis*(4-chlorophenyl) ethylene and 3 cc. of chromic acid – acetic acid oxidation mixture. The mixture was heated for 30 min. on the edge of the steam bath and was diluted with water. The precipitated solid was collected on a filter, m.p. 144° to 145° C. The melting point of the mixture of the product taken with an authentic sample of 4,4′-dichlorobenzophenone showed no depression.

In a similar manner the oil was oxidized to give 2,4′-dichlorobenzophenone and some 4,4′-dichlorobenzophenone.

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SULPHURIC ACID AS A REARRANGEMENT MEDIUM FOR SOME ALPHA-DIPHENYLTRICHLOROETHANES[1]

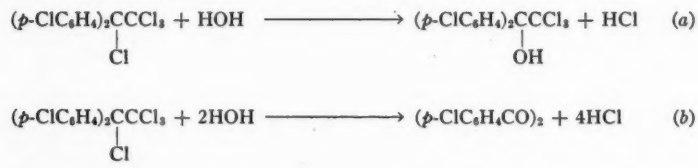
By G. T. Barry[2] and R. Boyer

Abstract

The compounds 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane and 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane (DDT) are reported to rearrange to 4,4′-dichlorobenzil by the catalytic action of sulphuric acid. Two proposed mechanisms for this conversion are discussed. Attempts to rearrange other substituted alpha-diphenyltrichloroethanes to the corresponding benzils were unsuccessful.

Introduction

In the preparation of homologues of *p,p′*-DDT, a rearrangement was observed to occur when either 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane (*p,p′*-DDT) or 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane was heated with sulphuric acid. The rearrangement product was identified as 4,4′-dichlorobenzil, I (*b*), and none of the expected 1,1,1-trichloro-2-hydroxy-2,2-*bis*(4-chlorophenyl) ethane compound I (*a*), could be isolated.



$$(p\text{-}ClC_6H_4)_2CCCl_3 + HOH \longrightarrow (p\text{-}ClC_6H_4)_2CCCl_3 + HCl \quad (a)$$

(Cl and OH)

I

$$(p\text{-}ClC_6H_4)_2CCCl_3 + 2HOH \longrightarrow (p\text{-}ClC_6H_4CO)_2 + 4HCl \quad (b)$$

(Cl)

No previous reports of rearrangements of diaryl polyhalogen compounds to substituted benzils could be found in the literature. However, closely related compounds have been reported to give rearrangement products upon treatment by various reagents. Elbs (4, 5) and Forster (5), in 1889, showed the rearrangement of a few alpha-diphenyltrichloroethane compounds to stilbenes. Later, Harris (12, 13) and Frankforter (13) converted a few polyhalogen compounds to rearranged unsaturated products using sodium or sodium ethylate in benzene. More recently, Forrest (8), Fleck (7), and Walton (20) have reported the rearrangement of *p,p′*-DDT or of 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane under various conditions.

The isolated conversions of a few compounds of a series is not without parallel in intramolecular conversions. Both Favorsky (6) and James and Lyons (15) have shown this phenomenon to occur in other series of compounds. This specificity appears complex, and special investigation for determining the optimum conditions in each case is required.

[1] *Manuscript received February 4, 1948.*
Contribution from the Organic Chemistry Laboratory, McGill University, Montreal, Que.

[2] *Holder of a Studentship and Fellowship under the National Research Council of Canada, 1944-1945. At present: National Institute of Health Fellow, Rockefeller Institute for Medical Research, New York, New York.*

The extent of the rearrangement to be described also appears limited to only a few compounds of the series. At 90° C. the transformation of 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane with 96% sulphuric acid proceeds slowly, and no appreciable reaction takes place with DDT under these conditions. At acid concentrations of 100%, containing considerable amounts of sulphur trioxide in solution, no water insoluble 4,4′-dichlorobenzil was obtainable after dilution of the reaction mixture with water. If the rearrangement does take place with high acid concentrations, then it is conceivable that the product is sulphonated. With 98% sulphuric acid 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane is readily converted to 4,4′-dichlorobenzil, but 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane is converted in only small yield to the same product with 100% acid.

No substituted benzil derivatives were obtained from the following compounds: 1,1,1-trichloro-2,2-*bis*(4-tolyl)ethane, 1,1,1-trichloro-2,2-diphenylethane, 1,1,1-trichloro-2-phenyl-2-(4-chlorophenyl)ethane, 1,1,1-trichloro-2,2-*bis*(4-bromophenyl)ethane, 1,1,1-trichloro-2,2-*bis*(4-chloro-3-nitrophenyl)-ethane, 1,1-dichloro-2,2-*bis*(4-chlorophenyl)ethylene, 1,1-*bis*(4-chlorophenyl)-ethylene, and 1,1-*bis*(4-tolyl)ethane. These compounds either did not react under the acid and temperature conditions employed, or, if the reaction did take place, no water insoluble products could be obtained upon dilution of the reaction mixture with water. In the latter case, sulphonation probably had taken place.

The proof of structure of the 4,4′-dichlorobenzil obtained from the degradation of the 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane and DDT was established by oxidation, analysis, and synthesis. A summation of the properties of the degradation product obtained compared with those of 4,4′-dichlorobenzil is shown in Table I.

TABLE I

COMPARISON OF PROPERTIES OF 4,4′-DICHLOROBENZIL AND DEGRADATION PRODUCT

Properties	4,4′-Dichlorobenzil	Degradation product
Molecular formula	$C_{14}H_8O_2Cl_2$	$C_{14}H_8O_2Cl_2$
Molecular weight	279	289, 290, 281
Oxidation product	4-Chlorobenzoic acid	4-Chlorobenzoic acid
Melting point	193° C. (16), 200° C. (18)	195–196° C.
Phenylhydrazone	178° C. (16)	178° C.
Color	Yellow	Yellow

The melting point of the mixture of the degradation product and 4,4′-dichlorobenzil (1) synthesized by another method showed no depression.

Discussion

Because of the close relationship between the rearrangement of 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane and 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane to the pinacol–pinacolone transformation, interest is stimulated as to the mechanism. To postulate a reasonable mechanism for the observed conversions is far more difficult than for a pinacol–pinacolone transformation, because of the loss of four atoms in the former molecule to only one atom in the latter.

Two mechanisms, *A* and *B*, are herein proposed for the observed rearrangements. The two mechanisms differ in that for one the alpha carbon atom of the side chain is initially attacked, while for the other the point of attack is the beta carbon atom (II).

$$\overset{\alpha\ \beta}{=CHCCl_3} \quad \text{and} \quad \overset{\alpha\ \beta}{=CClCCl_3} \qquad \text{II}$$

Any proposed mechanism must take into account the fact that the conversion of the DDT molecule appears to proceed only when 100% sulphuric acid is used, whereas the conversion of the alpha-chlorinated DDT molecule can be brought about to some extent with 96% sulphuric acid.

Mechanism A

If it is assumed that the initial attack is on the alpha carbon atom, then the mechanism could be represented as follows for 1,1,1-trichloro-2,2-*bis*-(4-chlorophenyl)ethane and 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane, respectively.

Step I $(ClC_6H_4)_2CHCCl_3 + H_2SO_4 \longrightarrow (ClC_6H_4)_2C(OH)CCl_3 + H_2O + SO_2$

$(ClC_6H_4)_2CClCCl_3 + H_2SO_4 \longrightarrow (ClC_6H_4)_2C(OH)CCl_3 + HCl + SO_3$

Step II $(ClC_6H_4)_2C(OH)CCl_3 + 2H_2SO_4 \longrightarrow (ClC_6H_4)_2\overset{+}{C}CCl_3 + OH_3^+ + 2HSO_4^-$

Step III $(ClC_6H_4)_2\overset{+}{C}CCl_3 \longrightarrow ClC_6H_4\underset{+}{C}ClCCl_2C_6H_4Cl$

Step IV $ClC_6H_4\underset{+}{C}ClCCl_2C_6H_4Cl + OH^- \longrightarrow ClC_6H_4C(OH)ClCCl_2C_6H_4Cl$

$ClC_6H_4COCCl_2C_6H_4Cl + HCl$

Step V $ClC_6H_4COCCl_2C_6H_4Cl + HOH \longrightarrow ClC_6H_4COCOC_6H_4Cl + 2HCl$

The oxidation of the tertiary hydrogen atom of DDT in Step I is a point requiring further elucidation. It would be expected that at least some conversion should take place with 96% sulphuric acid, but this is not the case. A small amount of 4,4′-dichlorobenzil can be obtained only if either mercuric or ferric chloride is added as an oxidation catalyst. If this reaction is analogous to the decomposition of formic acid to carbon monoxide and water (11, p. 277) where the rate with 95% sulphuric acid is 100 times slower than with

100% acid, then this conversion must be considered to be an acid-catalyzed reaction which is inhibited by the base water. As the conversion of 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane to 4,4′-dichlorobenzil is slow even with 100% sulphuric acid, it is conceivable that if the rate were decreased to one-hundredth for 96% acid, no product would have been detected.

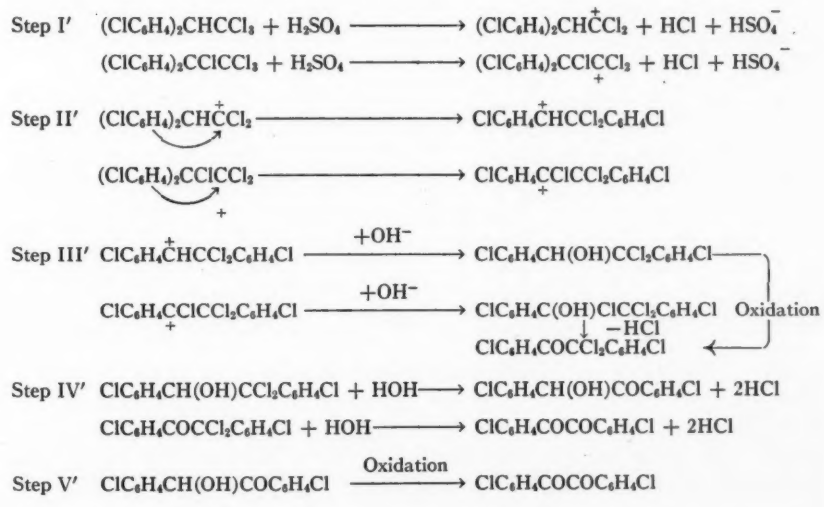
The hydrolysis or ionization of the tertiary aliphatic chlorine atom in 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane should proceed, as chlorine atoms attached to tertiary carbon atoms are usually labile. For example, triphenylmethylchloride is readily transformed to triphenylcarbinol, even with water. Triphenylcarbinol has been shown to form a carbonium ion in concentrated sulphuric acid (11, p. 54). Thus ion formation is considered reasonable for 1,1,1-trichloro-2-hydroxy-2,2-*bis*(4-chlorophenyl)ethane in Step II.

The rearrangement of the carbonium ion with an open sextet of Step III is in accord with present theory but its interpretation in this case is obscure because of the migration of two atom groups simultaneously.

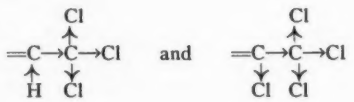
Both Steps IV and V are believed possible under the experimental conditions employed. An 80% solution of acetic acid has been shown to hydrolyze 1,1,2,2-tetrachloro-1,2-*bis*(4-chlorophenyl)ethane to 4,4′-dichlorobenzil by heating to 170° C. for six hours (16). Sulphuric acid was shown to convert 1,1,2,2-tetrachloro-1,2-diphenylethane to benzil by heating (17). Zinin (21) converted 1,2-diphenyl-2,2-dichloroethanone into benzil by heating with water.

Mechanism B

This alternate mechanism assumes the initial attack on the beta carbon atom of the side chain. Schematically, the mechanism for the conversions of 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane and 1,1,1,2-tetrachloro-2,2-*bis*-(4-chlorophenyl)ethane is outlined below.



This mechanism depends upon the ionization of an aliphatic chlorine atom from the trichloromethyl group of both compounds. On the basis of electronic theory, the tertiary chlorine atom on the tertiary carbon atom in the 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane molecule, because of its $(+I_e)$ inductive effect, should tend to deactivate the chlorines in the trichloromethyl group in contrast to the trichloromethyl group in 1,1,1-trichloro-2,2-*bis*-(4-chlorophenyl)ethane (III).



A *B* III

As previously stated, Compound *B* is more easily converted to 4,4′-dichlorobenzil than Compound *A* (DDT), but this is not in agreement with a deactivation of the trichloromethyl group in the former molecule.

The possibility should be mentioned that if the viewpoint of Johnson is considered, then trichloromethyl group deactivation may not be a valid postulation. This author states, "It is evident that there are certain special types of organic reactions which cannot be dealt with adequately on the basis of the four electronic concepts—[electromeric, mesomeric, inductive and inductomeric]. When a reaction involves redistribution of atomic nuclei among themselves (tautomerism and intramolecular rearrangements) the introduction of additional special principles is required." (9).

If Step I′ is accepted, the ensuing steps would seem reasonable. The 4-chlorophenyl shift of Step II′, the hydroxyl group addition in Step III′, and the aliphatic chlorine hydrolysis of Step IV′, should all theoretically proceed without difficulty. Step V′, which involves oxidation of 4,4′-dichlorobenzoin, is possible though none of this material was isolated from the reaction mixture.

Other possible mechanisms may be mentioned briefly. If it is assumed that all the aliphatic chlorines in the trichloromethyl groups are hydrolyzed before the rearrangement takes place, then *bis*-4,4′-dichlorophenylacetic acid should be obtained from 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane and 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane, respectively (IV).

$$(ClC_6H_4)_2CHCCl_3 + 3HOH \longrightarrow (ClC_6H_4)_2CHCOOH + 3HCl + H_2O$$
$$\downarrow \text{Oxidation}$$
$$(ClC_6H_4)_2C(OH)COOH$$
$$(ClC_6H_4)_2CClCCl_3 + 4HOH \longrightarrow (ClC_6H_4)_2C(OH)COOH + H_2O + 4HCl \qquad \text{IV}$$

Further hydrolysis or oxidation should give the 2-hydroxy-2,2-*bis*(4-chlorophenyl)acetic acid derivative. If this were the reaction mechanism, then it should be possible to convert the above acid into 4,4′-dichlorobenzil with sulphuric acid. The benzilic acid derivative was prepared but it was found impossible to convert it into 4,4′-dichlorobenzil with 96% sulphuric acid.

Alternately, it may be assumed that the reaction route lies in the initial loss of hydrogen chloride from 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane, or of chlorine from 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane, to give the unsymmetrical olefin (V). However, 1,1-dichloro-2,2-*bis*(4-chlorophenyl)-ethylene, the intermediate in such a rearrangement, is not converted to 4,4′-dichlorobenzil with either 98% or 100% sulphuric acid.

$$(ClC_6H_4)_2CHCCl_3 \longrightarrow (ClC_6H_4)_2C{=}CCl_2 + HCl$$
$$(ClC_6H_4)_2CClCCl_3 \longrightarrow (ClC_6H_4)_2C{=}CCl_2 + Cl_2 \qquad V$$

Any mechanism involving the rupture of the molecule into a benzoyl fragment capable of coupling to give 4,4′-dichlorobenzil is not considered likely, as the yield of the substituted benzil in the rearrangement of 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane was 56%. Should two benzoyl groups couple, the yield could not exceed 50%.

Because of insufficient data, neither proposed mechanism conclusively explains the observed rearrangement of these two polyhalogen compounds. The rearrangement of 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane to 4,4′-dichlorobenzil apparently involves intramolecular oxidation, reduction, and hydrolytic processes, and is best explained by Mechanism *A*. The transformation of 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane to 4,4′-dichlorobenzil involves intermolecular oxidation–reduction as well as intramolecular oxidation–reduction with hydrolytic processes, and can perhaps best be explained by Mechanism *B*.

Experimental

Action of Sulphuric Acid on 1,1,1,2-Tetrachloro-2,2-bis(4-chlorophenyl)ethane

Into a 200 cc. round bottomed flask were placed 11 gm. of 98% sulphuric acid and 2.0 gm. (0.0051 mole) of 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)-ethane (10). The flask and contents were thoroughly shaken and heated on the steam cone for 14 hr. at 90° C., cooled, diluted with 50 cc. of water, and the precipitated product collected on a filter. The material was recrystallized from 95% ethanol), m.p. 194° to 195° C.; a second recrystallization, m.p. 195° to 196° C. Further recrystallizations from ethanol, chloroform, or acetic acid did not raise the melting point. The weight of the product was 0.8 gm., which is a 56% yield of 4,4′-dichlorobenzil. Calc. for $C_{14}H_8O_2Cl_2$: C, 60.21; H, 2.86; O, 11.49; Cl, 25.44%. Found: C, 60.6; 60.6; H, 3.00, 2.78; Cl, 25.25, 25.35, 25.45%. Molecular weight in acetone, calc., 279; found, 289, 290, 281.

The melting point of the mixture of the product and 4,4′-dichlorobenzil (1) synthesized by another method showed no depression.

Action of Sulphuric Acid on 1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethane

Into a 200 cc. round bottomed flask were placed 3.54 gm. (0.01 mole) of 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane and 30 gm. of 100% sulphuric acid. The mixture was thoroughly shaken, heated on the steam bath at 90° C.

for seven hours, cooled, and diluted with 150 cc. of water. The precipitated product was collected on a filter and dissolved in 95% ethanol. On partial cooling of the hot ethanol solution some fine yellow crystals precipitated, m.p. 180° to 190° C. The solution was filtered warm before any unchanged starting material (DDT) crystallized from the solution. The product was recrystallized from 95% ethanol, m.p. 193° C. The melting point of the mixture of the product and the material obtained from the action of 98% sulphuric acid on 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane showed no depression. The yield of 4,4′-dichlorobenzil was quite small.

No 4,4′-dichlorobenzil could be obtained by the action of 98% sulphuric acid on 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane.

Experiments Performed to Prove the Structure of the 4,4′-Dichlorobenzil

1. *Oxidation with Alkaline Hydrogen Peroxide* (19, p. 142)

Into a 250 cc. Erlenmeyer flask were placed 7 cc. of 5% sodium hydroxide solution and 20 cc. of 3% hydrogen peroxide. The solution was warmed on the steam bath to 65–70° C. and 0.105 gm. of the product obtained from the reaction of sulphuric acid on 1,1,1,2-tetrachloro-2,2-*bis*(4-chlorophenyl)ethane was added. About 30 cc. of 95% ethanol was added to make the solution homogeneous. An additional 10 cc. of 3% hydrogen peroxide was added and heating continued for about 15 min. The yellow solution soon became colorless; this indicated that the oxidation was completed. The product was precipitated with dilute hydrochloric acid, collected on a tared sintered glass crucible, dried in the oven at 100° C. for one hour, and weighed. The weight was 0.0726 gm., giving a 61.5% yield of 4-chlorobenzoic acid, m.p. 240° C. The melting point of the mixture of the oxidation product and an authentic sample of 4-chlorobenzoic acid showed no depression.

A similar oxidation of an authentic sample of 4,4′-dichlorobenzil gave 4-chlorobenzoic acid in 71% yield.

2. *Mono Oxime* (19, p. 167)

Into a 250 cc. Erlenmeyer flask were placed 1.5 cc. of 5 *M* hydroxylamine hydrochloride and 1.5 cc. of 5 *M* sodium acetate. About 0.1 gm. of the rearrangement product and 10 cc. of 95% ethanol were added to the solution and heated under reflux for three hours. The solution was cooled, and the product was precipitated with water and collected on a filter, m.p. 133° C. The product was recrystallized from an ethanol and water solution, m.p. 142° C. Further recrystallization did not raise the melting point. Calc. for $C_{14}H_9O_2NCl_2$: Cl, 24.13%. Found: Cl, 24.04, 24.07%.

3. *Mono Phenylhydrazone* (19, p. 64)

Into a 250 cc. Erlenmeyer flask were placed 0.554 gm. (0.038 mole) of phenylhydrazine hydrochloride, 1.5 cc. of 5 *M* sodium acetate solution, and 0.27 gm. of the rearrangement product dissolved in 10 cc. of 95% ethanol.

The solution was heated under reflux for three hours, cooled, and the sides of the flask rubbed with a rubber policeman until crystallization took place. The product was collected on a filter, m.p. 178° C.; recrystallization from 95% ethanol gave no rise of melting point. The melting point of the mixture of the product and the starting material was taken and gave a large depression. The deep mustard yellow phenylhydrazone weighed 0.35 gm., giving a 90% yield. The melting point of the mixture of the product and the phenylhydrazone derivative prepared from an authentic sample of 4,4′-dichlorobenzil showed no depression.

4. *Quinoxaline* (14)

Into a 125 cc. Erlenmeyer flask were placed 150 mgm. of the rearrangement product and 5 cc. of glacial acetic acid. To this solution was added 50 mgm. of *o*-phenylenediamine, and the whole was heated under reflux for five hours on the steam bath, and cooled. Water was added to the solution until a state of incipient cloudiness was reached. The white precipitate was collected on a sintered glass crucible and dried for a few hours by the water aspirator, m.p. 185° C. No rise in melting point was obtained on recrystallization from 95% ethanol. The weight of the product was 48 mgm., giving a 25% yield of the quinoxaline.

Action of Sulphuric Acid on 1,1-Dichloro-2,2-bis(4-chlorophenyl)ethylene

Into a 50 cc. round bottomed flask were placed 25 gm. of 98% sulphuric acid and 1.59 gm. (0.005 mole) of 1,1-dichloro-2,2-*bis*(4-chlorophenyl)-ethylene (2); the mixture was heated on the steam bath for 15 hr., cooled, diluted with water, and filtered, m.p. 88° to 89° C. The melting point of the mixture of the product and the starting material showed no depression.

A repetition of this experiment with 100% sulphuric acid, and heating for 46 hr. at 90° C. on the steam bath resulted in the recovery of the reactant unchanged.

Attempted Conversion of 2-Hydroxy-2,2-bis(4-chlorophenyl)acetic Acid to 4,4′-Dichlorobenzil

One gram of oily 2-hydroxy-2,2-*bis*(4-chlorophenyl)acetic acid (3) was mixed in a 50 cc. round bottomed flask with 10 gm. of 96% sulphuric acid, heated on the steam bath for 10 hr., cooled, and diluted with water. The precipitate was collected on a filter and found to be quite soluble in ethanol. No 4,4′-dichlorobenzil was obtained from the ethanol solution.

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THE OXIDATION OF MERCAPTANS BY POTASSIUM PERSULPHATE IN HOMOGENEOUS SOLUTION[1]

R. L. EAGER[2] AND C. A. WINKLER

Abstract

In the homogeneous oxidation of mercaptans by potassium persulphate in concentrated acetic acid, the rate of disappearance of potassium persulphate during an experiment is first order with respect to the measured persulphate concentration. The rate constant is independent of the kind of mercaptan used, and is independent of mercaptan concentration over a wide range of mercaptan concentrations. The rate constant falls off, however, at low mercaptan concentrations, this falling-off being less pronounced if the rate is reduced by the addition of salts. The mercaptan concentration at which the rate constant, calculated from persulphate disappearance, becomes independent of mercaptan concentration increases as the temperature is increased. A salt effect prevails, the rate constant being decreased with increased potassium ion concentration. The equivalent conductance of solutions of potassium persulphate in the solvent used shows a behavior on dilution which indicates that potassium persulphate is incompletely ionized in the solvent. A mechanism is proposed for the reaction, in which it is assumed that dissociation of persulphate ions into sulphate free radicals is rate-controlling, with an activation energy of the order 26,000 cal. per mole.

Introduction

The well known use of potassium persulphate as 'catalyst' and of mercaptans as modifiers in emulsion polymerization has made studies on the interaction of these compounds of fundamental interest and importance. To avoid the many complications attending the use of emulsion systems, it is obviously desirable to investigate the oxidation of mercaptans by potassium persulphate in a homogeneous system. The present paper discusses the results of such a study.

Experimental and Results

Preliminary search for a solvent revealed that suitable amounts of potassium persulphate and of mercaptans up to *n*-dodecylmercaptan could be brought into solution in concentrated acetic acid (80 ml. glacial acid: 10 ml. water). Blank experiments at each temperature used in studying the oxidation of the mercaptans showed that the rate of disappearance of potassium persulphate alone in the mixed solvent was well within the experimental error of the oxidation studies.

Reaction mixtures were contained in 500 ml. glass-stoppered Erlenmeyer flasks, immersed in suitable thermostats, the temperatures of which were controlled within $\pm 0.02°$ C.

A solution of the desired amount of potassium persulphate in 225 ml. of mixed solvent was brought to the temperature of the thermostat, after which the desired amount of mercaptan was added with a pipette. The course

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of the reaction was followed by withdrawing a sample periodically and analyzing for the potassium persulphate content by the procedure of Kolthoff *et al.* (3), with slight modification. The sample was added to 100 ml. of 0.6 *N* sulphuric acid, an excess of ferrous sulphate added, and the solution allowed to stand for a sufficient length of time for the reaction between potassium persulphate and ferrous ion to go to completion. The solution was then back titrated with 0.005 *N* ceric sulphate, using 2 ml. of 0.005 *M* solution of *o*-phenanthroline as indicator. Approximately one hour was found necessary for complete oxidation of the ferrous ion in water, but the presence of acetic acid reduced this time to 30 – 40 min.

The mercaptans used were kindly supplied by Polymer Corporation, Sarnia. The *n*-butyl and *n*-octyl mercaptans had been purified in the Polymer Corporation Laboratories and were used without further purification. The *n*-dodecyl mercaptan was distilled at 20 mm. pressure, a middle fraction with a boiling range 150.4° to 151.0° C. being collected for experimental purposes.

Order of Reaction in a Single Experiment

The disappearance of potassium persulphate during a given experiment was found to be first order with respect to the measured persulphate concentration, as shown by the typical plot of data for the oxidation of *n*-dodecyl mercaptan shown in Fig. 1. The first order relation was found to hold for all the experiments made, except those with low mercaptan concentrations, which will be discussed later.

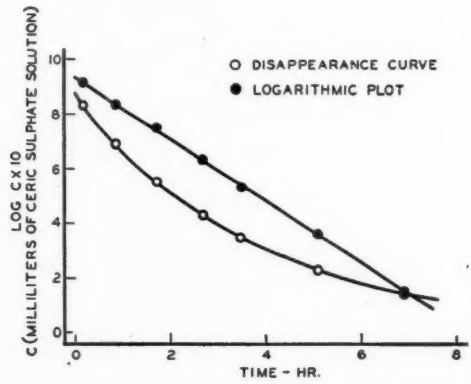

FIG. 1. *Typical curve for disappearance of potassium persulphate in a single experiment.*

In a given experiment the rate constant was found from the slope of the line obtained by plotting the logarithm of the measured persulphate concentration against time, as in Fig. 1. While the rate constant is first order in a given experiment, its value was found to vary with the initial persulphate concentration, and in this sense is not a first order rate constant. It will therefore be designated simply as the rate constant (k_1) rather than first order rate constant.

Effect of Mercaptan Concentration on Rate of Disappearance of Potassium Persulphate

Using *n*-dodecyl mercaptan, the effect of mercaptan concentration on the rate of disappearance of potassium persulphate was determined at 25° and 35° C. The data are summarized in Figs. 2 and 3. It is immediately evident

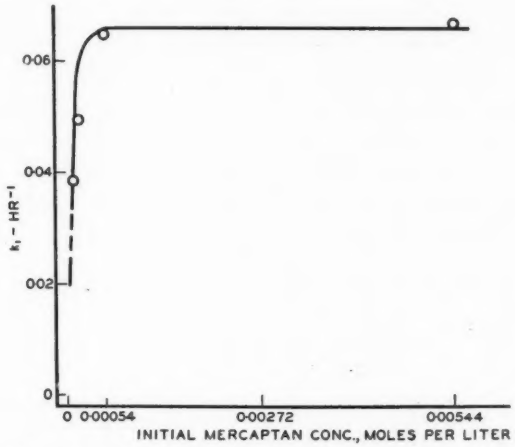

FIG. 2. *Variation of k_1 with n-dodecyl mercaptan concentration. Initial potassium persulphate concentration, 0.00153 mole per liter; temperature, 25.00 ± 0.01 °C.*

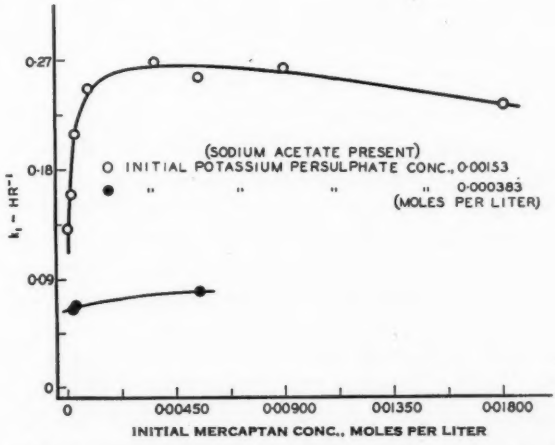

FIG. 3. *Variation of k_1 with mercaptan concentration; temperature, 35.00 ± 0.01 °C.*

that the rate constant for potassium persulphate disappearance is essentially independent of mercaptan concentration over a considerable range of mercaptan concentrations, but shows a marked falling-off at sufficiently low

mercaptan concentrations. In the region of low mercaptan concentrations the reaction–time curves are first order with respect to persulphate only in the early stages, beyond which the rate constants fall off. It should be noted further that the mercaptan concentration at which the value of k_1 begins to fall off is higher at 35° C. than at 25° C. by a factor of approximately four.

Effect of Mercaptan Structure on Rate of Disappearance of Potassium Persulphate

The effect of mercaptan structure on the rate of disappearance of potassium persulphate (0.00153 mole per liter) was determined by extending the investigation at 35° C., to include *n*-octyl and *n*-butyl mercaptans, using mercaptan concentrations in the range where the rate constant is little influenced by mercaptan concentration. With *n*-octyl mercaptan (0.0076 mole per liter) the value of k_1 (hr.$^{-1}$) was 0.25, while with *n*-butyl mercaptan (0.0121 mole per liter) the value was 0.32. These are to be compared with a value for *n*-dodecyl mercaptan (0.0091 mole per liter) of 0.26. The somewhat higher value of k_1 obtained for *n*-butyl mercaptan is probably to be attributed to analytical difficulties. With this mercaptan most of the unreacted material remained in solution in the analytical mixture (instead of emulsifying) where appreciable attack by ceric sulphate might occur, to increase the back titration and give an apparently low potassium persulphate content. Reaction of ceric sulphate with *n*-butyl mercaptan was indicated by reversion of the end point almost immediately after completion of the titration. The data presented above would indicate that the structure of the mercaptan used has no significant influence on the rate of disappearance of potassium persulphate at a given temperature.

Effect of Potassium Persulphate Concentration on the Rate of its Disappearance

The effect of initial concentration of potassium persulphate on its rate of disappearance was determined at *n*-dodecyl mercaptan concentrations in the range where the rate constant is essentially independent of mercaptan concentration. The data for three different temperatures, recorded in Table I, show that the rate constant at a given temperature decreases as the initial concentration of potassium persulphate is increased.

Effect of Added Salts on the Rate of Disappearance of Potassium Persulphate

The decrease in k_1 for disappearance of potassium persulphate with increase in its initial concentration is most readily explained as a salt effect. To determine the extent of possible salt effect on the reaction rate, experiments were made in which various amounts of different salts were added to the reaction mixture. The results are plotted in Fig. 4. The concentrations of added salts are expressed in terms of the total concentration of potassium and sodium ions, including the potassium ions originally added as potassium persulphate.

In Expt. 9 the initial amount of potassium persulphate is four times that in Expt. 25. To the latter experiment, however, was added potassium hydrogen sulphate, a product of reaction when persulphate acts as an oxidizing agent (6).

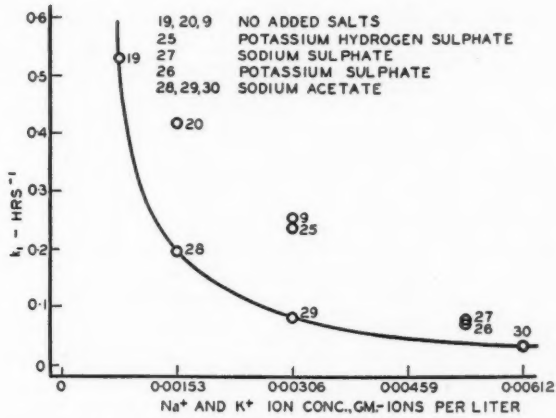

FIG. 4. *Variation of k_1 with added salts. Initial n–dodecyl mercaptan concentration, 0.00544 mole per liter, except in 20, where it is 0.00907 mole per liter; initial potassium persulphate concentration, 0.000383 mole per liter, except in 9, where it is 0.00153 mole per liter; temperature, 35.00 ± 0.01° C.*

The amount added was sufficient to bring the potassium hydrogen sulphate concentration up to that which would have prevailed had four times the initial amount of potassium persulphate been used, assuming complete reaction of the persulphate to potassium hydrogen sulphate. It will be noted that the rate constants in the two experiments were the same, indicating that potassium persulphate and its reaction product have the same salt effect.

In Expt. 26 the normal instead of the acid sulphate was added, the total potassium ion concentration being thereby increased by a factor of seven-fourths. The effect was to reduce the rate to about one-third the value where the acid salt was added. It seems plausible to attribute the decreased rate to increased potassium ion concentration rather than to a difference in added hydrogen ion, since it is unlikely that the small amount of salt added could influence significantly the hydrogen ion concentration in the solvent used. The addition of sodium sulphate gave an effect entirely similar to that of potassium sulphate. The effect of adding sodium acetate (Expts. 28, 29, 30) may therefore be taken as equivalent to the salt effect that would have been observed had potassium acetate been used (its deliquescence was a deterrent to its use). It will be convenient to discuss the salt effect later in terms only of potassium ions, although in the experimental work sodium salts have sometimes been used. It will be noted that with increasing amounts of sodium ion

the value of k_1 decreased progressively. From the remarks above, it is inferred that potassium ions would reduce k_1 correspondingly.

TABLE I

VARIATION OF THE RATE CONSTANT, k_1, WITH INITIAL CONCENTRATION OF POTASSIUM PERSULPHATE

Exp. No.	Initial *n*-dodecyl mercaptan concentration, mole/liter	Initial $K_2S_2O_8$ concentration, mole/liter	k_1, hr.$^{-1}$
Temperature = 25.00 ± 0.01° C.			
5	0.00544	0.000383	0.133
17	0.00544	0.000766	0.089
1	0.00544	0.00153	0.067
Temperature = 35.00 ± 0.01° C.			
18	0.00544	0.000248	0.601
19	0.00544	0.000383	0.530
20	0.00907	0.000766	0.418
10	0.00363	0.00153	0.267
9	0.00544	0.00153	0.255
Temperature = 45.00 ± 0.02° C.			
21	0.00544	0.000383	2.14
22	0.00544	0.000766	1.40
23	0.00544	0.00153	0.94

Effect of Initial Mercaptan Concentration on the Rate of Disappearance of Mercaptan in the Presence of Sodium Acetate

Data plotted in Fig. 3, for the effect of initial mercaptan concentration on the rate of disappearance of mercaptan in the presence of sodium acetate, show that the falling-off of k_1 at low mercaptan concentrations is much less pronounced under these conditions than when no salt is added (cf. Figs. 2 and 3).

Effect of Sulphate Ion on the Rate of Disappearance of Potassium Persulphate

Where the sulphate ion concentration had been increased four times, as a result of using potassium sulphate (Expts. 26 and 27, Fig. 4) instead of sodium acetate to bring the total sodium and potassium ion concentration to a given

level, the value of k_1 was approximately doubled. This would suggest that the presence of sulphate ion results in a higher value of k_1. More direct evidence for this is given by comparison of Expts. 9 and 29, and Expts. 20 and 28, where it will be seen that for given potassium ion concentration, a higher sulphate ion concentration corresponds to a larger value of k_1.

Experiments with the addition of sulphuric acid at constant potassium ion concentration, the data for which are plotted in Fig. 5, show that increased 'effective' sulphate ion concentration does, in fact, result in increased rate of

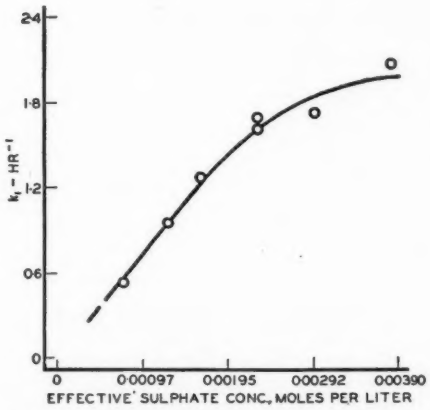

FIG. 5. *Variation of k_1 with sulphuric acid. Initial n-dodecyl mercaptan concentration, 0.00544 mole per liter; initial potassium persulphate concentration, 0.000383 mole per liter; temperature, 35.00 ± 0.01° C.*

reaction (the 'effective' sulphate ion concentration is the total sulphate ion concentration that would exist if all the potassium persulphate initially present were converted to its equivalent of sulphate). The effect on the rate is linear for small acid concentrations but falls off at higher concentrations.

Effect of Dilution on the Equivalent Conductance of Potassium Persulphate in Concentrated Acetic Acid Solutions

A salt effect such as that described previously may result from incomplete ionization of a salt, the ions of which are involved in the reaction. Measurement of the equivalent conductance of potassium persulphate for various concentrations in the acetic acid solvent at 25° C. gave the data plotted in Fig. 6. For comparison, data are also plotted for sodium chloride in water (1), an example of a completely ionized electrolyte, and for acetic acid in water (2), an example of a slightly ionized electrolyte. The marked increase in equivalent conductance with dilution leaves little doubt that potassium persulphate is only partially ionized in the concentrated acetic acid used as solvent.

Calculation of Activation Energies

From the rate constants at different temperatures, activation energies may be calculated, as in Table II, by applying the familiar Arrhenius equation. The data indicate an average value for the activation energy of approximately 26,000 cal. per mole.

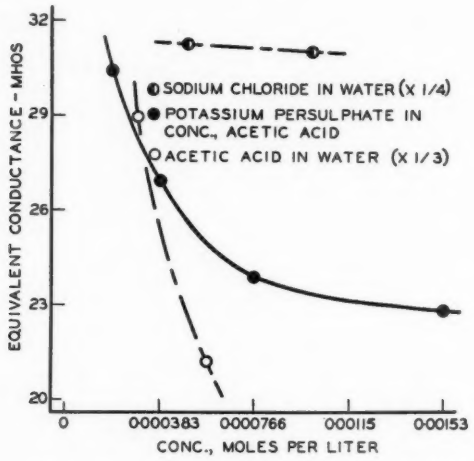

FIG. 6. *Variation of the equivalent conductance of potassium persulphate with concentration; composition of solvent, 26.26 gm. of water and 208.7 gm. of glacial acetic acid; temperature, 25.00 ± 0.01° C.*

Relative Molar Disappearance of Potassium Persulphate and Mercaptan

An attempt was made to analyze for mercaptan disappearance using the amperometric procedure of Kolthoff and Harris (4). Sufficient ammonium hydroxide was added to neutralize the acetic acid present in the sample. The end point was very indefinite, however, and estimation of mercaptan was abandoned.

The relative over-all consumptions of potassium persulphate and *n*-dodecyl mercaptan was found as follows. An excess of persulphate was used and the experiment allowed to continue until the potassium persulphate concentration had reached a steady value. If it is assumed that all the mercaptan had then been consumed, the relative number of moles of persulphate and mercaptan that have disappeared can then be calculated. The data obtained are in Table III.

It should be noted that the observed ratio of approximately 3 for the relative consumptions of persulphate and mercaptan might be true only for the later stages of reaction, if more than one oxidation step is involved in production of the final products. It should be noted also that in these experiments the

potassium persulphate concentrations were in excess of the mercaptan concentrations, whereas in the experiments from which the rate constants were determined the reverse was usually true.

TABLE II

CALCULATION OF ACTIVATION ENERGIES

Initial *n*-dodecyl mercaptan concentration = 0.00544 mole per liter

Exp. No.	Temp., T, °K.	Initial potassium persulphate concentration, mole/liter	Added compound, mole/liter	k_1	Activation, energy, E, cal./mole
*36 and 37	308	0.000383	H_2SO_4 (0.00153)	1.64	26,100
33	298	0.000383	H_2SO_4 (0.00153)	0.392	
21	318	0.000383		2.14	27,100
19	308	0.000383		0.530	25,200
5	298	0.000383		0.133	
22	318	0.000766		1.40	23,400
20	308	0.000766		0.418	28,200
17	298	0.000766		0.089	
23	318	0.00153		0.939	25,400
9	308	0.00153		0.255	24,400
1	298	0.00153		0.067	

* *Results for Expts. 36 and 37 averaged.*

TABLE III

MOLAR RATIO OF CONSUMPTION OF POTASSIUM PERSULPHATE TO *n*-DODECYL MERCAPTAN

Temperature, °C.	Initial *n*-dodecyl mercaptan, moles	Potassium persulphate consumed, moles	Ratio moles potassium persulphate to *n*-dodecyl mercaptan consumed
25.00 ± 0.01	0.0000402	0.000123	3.07
35.00 ± 0.01	0.0000805	0.000226	2.81
45.00 ± 0.02	0.0000805	0.000236	2.93

Discussion

The observation that the rate constant for potassium persulphate disappearance is independent of the kind of mercaptan and its concentration, at higher concentrations, implies that under such conditions the rate is governed

by a slow reaction involving potassium persulphate to produce one or more reactive species capable of comparatively rapid oxidation of mercaptan. The dissociation of $S_2O_8^=$ ion into sulphate free radicals, $SO_4^{\cdot-}$ as suggested by Evans and Baxendale (5) would seem to offer a simple explanation of the behavior. Such dissociation might well be expected to be slow compared with subsequent reaction of the radicals formed. However, since the disappearance of potassium persulphate was found to be negligible in the absence of mercaptan, the dissociation reaction apparently is reversible, i.e.,

$$S_2O_8^= \underset{k^\circ_{-1}}{\overset{k^\circ_1}{\rightleftharpoons}} 2\,SO_4^{\cdot-},$$

where the recombination reaction may be assumed to be comparatively rapid, though hindered to some extent by electrostatic repulsion.

On this basis, a mechanism may be suggested as follows:

(1) $$S_2O_8^= \underset{k^\circ_{-1}\text{ (fast)}}{\overset{k^\circ_1\text{ (slow)}}{\rightleftharpoons}} 2\,SO_4^{\cdot-}$$

(2) $$SO_4^{\cdot-} + RSH \xrightarrow{k^\circ_2\text{ (fast)}} RS^{\cdot} + H^+ + SO_4^=$$

(3) Further fast reactions of $RS^{\cdot}$ with themselves or sulphate free radicals or solvent.

Reaction of $SO_4^{\cdot-}$ free radicals with acetic acid to form $-CH_2COOH$ radicals or with water to form $OH^{\cdot}$ radicals would not seem to be important under the conditions used since, in the absence of mercaptan, potassium persulphate did not disappear at an appreciable rate in the acetic acid – water solvent.

If Step (2) is sufficiently fast relative to Step (1), as with excess mercaptan, the equilibrium in (1) will be inoperative and the rate of the over-all reaction should then be proportional to the concentration of $S_2O_8^=$ and independent of the kind and concentration of mercaptan. As the mercaptan concentration is decreased, a condition will eventually be reached where the rate of reaction between mercaptan and $SO_4^{\cdot-}$ radicals will be comparable with the rate of formation of $SO_4^{\cdot-}$ radicals. Hence, at sufficiently low mercaptan concentrations the rate should become dependent on mercaptan concentration, as observed. Furthermore, if the rate of production of $SO_4^{\cdot-}$ radicals is reduced, e.g., by addition of salts, then the dissociation of $S_2O_8^=$ ions into $SO_4^{\cdot-}$ radicals should remain rate-controlling to lower mercaptan concentrations, and the less pronounced falling-off in rate observed at low mercaptan concentrations is explained. Conversely, if, as seems likely, the activation energy for the production of $SO_4^{\cdot-}$ radicals is greater than for their reaction with mercaptan, an increase of temperature should correspond to an increase in the mercaptan

concentration at which the rate of potassium persulphate disappearance becomes dependent on mercaptan concentration. This, too, is in accord with the observed behavior.

The proposed mechanism must also be examined in relation to the observed salt effect. Since a positive effect on the rate was observed with sulphuric acid, but a negative effect with sodium or potassium salts, it appears that increased ionic strength does not lead to a primary salt effect, which should be consistently positive or negative for a given reaction. On the other hand, the data obtained with added salts may be readily interpreted as a secondary salt effect, in which addition of, say, potassium ions reduces the concentration of the reactive $S_2O_8^=$ ions by forming a partially dissociated salt, while the addition of sulphate ion, by similarly forming a partially dissociated salt with potassium ions present, induces further dissociation of the persulphate to increase the concentration of reactive $S_2O_8^=$ ion.

In any given experiment the disappearance of potassium persulphate follows first order behavior down to a small fraction of the original amount of persulphate. Hence, if the original assumptions were correct, the potassium ion concentration must have remained constant. The potassium ion concentration could be kept approximately constant in a given experiment if the products of reaction, HSO_4^- or $SO_4^=$ form incompletely ionized salts with potassium ion in the solvent used, to about the same extent as $KS_2O_8^-$ and $S_2O_8^=$.

Since potassium persulphate behaves as a weak electrolyte in the system the following equilibrium (with constant K_1) must exist:

$$K_2S_2O_8 \rightleftharpoons 2\,K^+ + S_2O_8^= .$$

On the basis of preceding remarks, it now becomes possible to establish a relation between the equilibrium constant, K_1, the rate constant, k°_1, for decomposition of $S_2O_8^=$ into free radicals, and the observed rate constant k_1 for the reaction.

At high mercaptan concentrations the rate-controlling reaction is assumed, as before, to be

$$S_2O_8^= \xrightarrow{k^\circ_1} 2\,SO_4^-$$

for which

$$\frac{-d}{dt}[S_2O_8^=] = k^\circ_1\,[S_2O_8^=] .$$

The $S_2O_8^=$ ion concentration is, however, not equal to the measured potassium persulphate concentration, but is some fraction of it, i.e.

$$[S_2O_8^=] = f[K_2S_2O_8] ,$$

where f = fraction of the measured potassium persulphate existing as $S_2O_8^{=}$ ion. Hence,

$$\frac{-d}{dt}[K_2S_2O_8] = k°_1 f\,[K_2S_2O_8]$$

and $k°_1 f = k_1$ (observed first order rate constant for reaction). Also, if $[K_2S_2O_8]^*$ represents the concentration of undissociated potassium persulphate in solution, as compared with the measured value $[K_2S_2O_8]$, then

$$[K_2S_2O_8] = [K_2S_2O_8]^* + [S_2O_8^{=}],$$

while the value of K_1 is given by

$$\frac{[K^+]^2\,[S_2O_8^{=}]}{[K_2S_2O_8]^*} = K_1$$

or

$$[K_2S_2O_8]^* = \frac{[K^+]^2\,[S_2O_8^{=}]}{K_1}.$$

Therefore

$$[S_2O_8^{=}] = \frac{K_1[K_2S_2O_8]}{K_1 + [K^+]^2}$$

and

$$f = \frac{K_1}{K_1 + [K^+]^2}.$$

The rate expression may then be written

$$\frac{-d}{dt}[K_2S_2O_8] = \frac{k°_1 K_1}{K_1 + [K^+]^2}[K_2S_2O_8]$$

The relation between $k°_1$ and k_1 is then

$$k_1 = \frac{k°_1 K_1}{K_1 + [K^+]^2}$$

Hence to obtain $k°_1$ from k_1 the value of K_1 and the potassium ion concentration corresponding to given k_1 must be known. Unfortunately, data are not available by which such an estimate of $k°_1$ may be made from the measured values of k_1.

It should be noted, however, that the activation energy for the rate-controlling decomposition of $S_2O_8^{=}$ ions into SO_4^{-} radicals should be calculated using the ratio of $k°_1$ values at different temperatures rather than ratio of k_1 values as in Table II. However, ratio of k_1 values should be satisfactory providing the value of f remains essentially constant at the different temperatures used in evaluating the activation energy. Changes in f with temperature will depend on changes in the ionization constant of a weak electrolyte with tem-

perature, the magnitude of which is generally not large compared with variation of a specific rate constant with temperature. Hence, the activation energies reported in Table II are probably of the right order.

Assuming the mechanism discussed above, the activation energy for the reaction

$$SO_4^{\cdot-} + RSH \xrightarrow{k^\circ_2} RS + H^+ + SO_4^{=}$$

may be calculated as follows.

Sulphate free radicals will begin to accumulate in the solution when the mercaptan concentration has been reduced to a value such that the free radicals are no longer removed by mercaptan as fast as they are formed by dissociation of persulphate ions. This will be the condition at the mercaptan concentration at which the rate of disappearance of persulphate begins to be dependent on mercaptan concentration. It seems safe to assume that at this concentration the following relation holds for the results at 25° C. and 35° C.

$$\frac{k^\circ_{1_{25}}[S_2O_8^{=}]_{25}}{k^\circ_{1_{35}}[S_2O_8^{=}]_{35}} = \frac{k^\circ_{2_{25}}[SO_4^{\cdot-}]_{25}[RSH]_{25}}{k^\circ_{2_{35}}[SO_4^{\cdot-}]_{35}[RSH]_{35}}$$

If sulphate free radicals can just begin to accumulate in the solution at the point where the rate falls off, then at this point their concentration may be taken to be approximately the same at the two temperatures. Also, for the same concentration of potassium persulphate the value of f, the fraction of the persulphate existing as persulphate ions, is probably not much different at the two temperatures since ionization constants are not, as a rule, greatly affected by a 10° change of temperature. Hence the ratio $\frac{k^\circ_{1_{25}}}{k^\circ_{1_{35}}}$ may be replaced by the ratio $\frac{k_{1_{25}}}{k_{1_{35}}}$.

With these approximations, it is possible to write

$$\frac{k_{1_{25}}}{k_{1_{35}}} = \frac{k^\circ_{2_{25}}[RSH]_{25}}{k^\circ_{2_{35}}[RSH]_{35}} .$$

Substituting into this equation the values of k_1 for 25° C. and 35° C. and the values of the mercaptan concentration at which the rate of disappearance of persulphate begins to be dependent on mercaptan concentration, a value of 1.04 is obtained for the ratio $\frac{k^\circ_{2_{35}}}{k^\circ_{2_{25}}}$. The appropriate values of the mercaptan concentrations are obtained from Figs. 2 and 3. Substituting this value for the ratio of the rate constants into the Arrhenius relation, the activation energy for reaction of $SO_4^{\cdot-}$ radicals with mercaptan is found to be approximately 600 cal. per mole. This value is only a rough approximation, but it probably serves to indicate that the activation energy for the reaction between $SO_4^{\cdot-}$ radicals and mercaptan is quite low.

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ADSORPTION AND DECOMPOSITION OF NICKEL CARBONYL ON THE SURFACE OF RESPIRATOR CHARCOALS[1]

H. LEVERNE WILLIAMS[2]

Abstract

Nickel carbonyl is adsorbed by respirator charcoals without decomposition in the absence of oxygen. The amount adsorbed is reduced if the charcoal has previously adsorbed nickel carbonyl, carbon tetrachloride, phosgene, or arsine and has not been degassed thereafter. The adsorbed nickel carbonyl is oxidized rapidly by oxygen, liberating carbon dioxide, carbon monoxide, and leaving an amorphous deposit on the charcoal. This deposit is slightly more than half nickel, and does not yield an X-ray diffraction pattern. Adsorbed nickel carbonyl is decomposed thermally to give metallic nickel and carbon monoxide. The nickel is deposited in sufficient amounts to give an X-ray diffraction pattern.

Davis (5) reported that nickel carbonyl, passing through a bed of standard respirator charcoal, was decomposed quantitatively into nickel and carbon monoxide. McIntosh and Mungen (17) found that the resulting nickel impregnated charcoals had essentially the same arsine service times as the original charcoal. Pierce noted (19) that there was no relation between the naturally occurring nickel content of the charcoals and their catalytic activity as measured by arsine service times.

A brief X-ray diffraction study of respirator charcoal after exposure to nickel carbonyl was undertaken by Matthews (15). He examined a charcoal containing 4.1% nickel (McIntosh and Mungen (17)) and one containing 6.52% nickel (prepared by Mr. J. W. Hodgins of the National Research Council, Ottawa). Neither of these samples yielded an X-ray diffraction pattern characteristic of crystalline compounds. Under similar experimental conditions a distinct X-ray pattern for nickel was obtained from a synthetic mixture of charcoal and nickel powder containing 5% nickel. From this it was concluded that the nickel must deposit on the charcoal in particles too small to yield a diffraction pattern.

The properties of nickel carbonyl are summarized in many publications (see (7)). Its reactions are those of nickel and of the unsaturated carbonyl group, to form inorganic salts and organometallic complexes. Exposure of the liquid to air results in the formation of carbonates whose composition varies with the hygroscopicity of the atmosphere or medium. Nickel carbonyl may be decomposed thermally to yield nickel and carbon monoxide. Studies of the oxidation of nickel carbonyl indicated the formation of complex hydrated hydroxy carbonates of variable composition (2, 3, 6, 9, 10, 11, 12, 14, 18, 22). Thermal decomposition proceeds to an equilibrium unless the carbon monoxide is removed (2, 6, 7, 9, 16).

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One of the oxidation products of nickel carbonyl could be nickel carbonate. This is unstable at ordinary temperatures (3) and can be decomposed completely at 325° C. (20, 21) to form nickel oxide and carbon dioxide.

Apparatus

Three experimental systems were used. The first apparatus (Fig. 1) resembled that used by McIntosh and Mungen (17). The air passed through two drying towers containing calcium chloride and through the main flow-

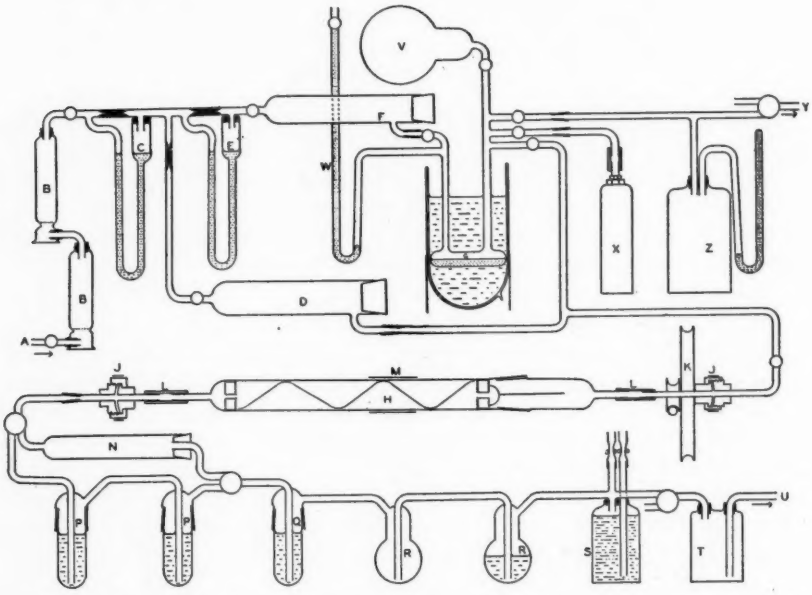

FIG. 1. *Flow system for tumbling charcoal in an atmosphere containing nickel carbonyl vapors.*

meter, after which the air was divided into two streams. The main portion of the air flow passed through a drying tube containing phosphorus pentoxide. The minor portion passed through a second flowmeter and a drying tube containing phosphorus pentoxide and into the carburetor, where it picked up nickel carbonyl. The recombined air streams then were led into the tumbler composed of a long glass tube mounted on unions so that it rotated smoothly. A pulley was mounted on one union and connected by a belt to a gear reducer and motor assembly. The long tumbler tube was connected to the unions with rubber tubing to absorb the whip, and was supported further by a glass sleeve at the middle. The charcoal in the tumbler was kept confined by corks with holes covered by brass screen, and kept stirred by means of a wire spiral on the inside of the glass.

After passing through the tumbler the air stream went through either a Hopcalite – calcium chloride tube or through traps containing test solutions for carbon monoxide or nickel carbonyl. A further test trap followed, then a trap containing 6 *N* nitric acid to destroy any nickel carbonyl. The air stream passed through a pressure regulator, a cushioning volume, and a water aspirator. The carburetor assembly was made of glass and was vacuum tight. It was connected to another cushioning volume, a manometer, the nickel carbonyl cylinder, and to an Hyvac pump through a cushioning volume.

The carburetor was charged by evacuating the system, opening the valve to the cylinder of nickel carbonyl, and allowing the carbonyl to distill into the carburetor, which was cooled in a dry ice–acetone mixture. The system was then returned to atmospheric pressure and room temperature before the air was allowed to flow through. The flows through the flowmeters were adjusted so that the nickel carbonyl was present in the combined air streams to the extent of approximately 1 part per 100.

In the second system (Fig. 2), a static system, the charcoal was placed in a brass screen cell in a chamber. This chamber was so connected to two traps and the Hyvac pump system that nickel carbonyl could be condensed in either

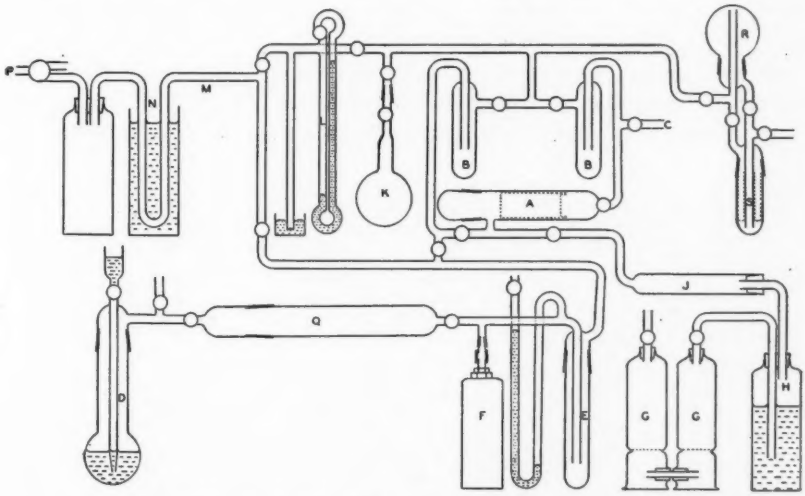

FIG. 2. *Apparatus for adsorbing nickel carbonyl on the surface of charcoal and decomposing the carbonyl.*

trap and then distilled from the one trap to the other through the charcoal in the cell. This system was connected in turn to an oxygen cylinder and to a carbon monoxide and hydrogen chloride generator through the same trap that joined the nickel carbonyl cylinder to the system. Dry air could be admitted to the chamber after passing through a train composed of two towers containing calcium chloride, a bubbler containing concentrated sulphuric acid,

and a tube containing potassium hydroxide pellets. A vapor density bulb was connected to the system, as was also a pyrolysis system. This system was self-circulating, with a bulb and a trap. The gas passed from the bottom of the bulb through a tube leading to the bottom of the trap, thence up through the trap, and through a tube to the top of the bulb. This trap contained a cylindrical brass cell that held the charcoal, and it was surrounded by either a constant temperature bath or a furnace. The whole system was evacuated through a manometer system, a pyrolysis tube, a cooling trap, and a cushioning volume to a Hyvac.

Carbon monoxide and hydrogen chloride were prepared by dropping formic acid or hydrochloric acid respectively into concentrated sulphuric acid and passing the gas through a long tube containing calcium chloride and a trap cooled by liquid air or by a dry ice – acetone mixture. The nickel carbonyl was introduced by condensing it in one of the traps cooled in a dry ice – acetone mixture after the system had been evacuated. Carbon dioxide was introduced by placing dry ice in a trap that was demountable and cooling it in liquid air while evacuating the system, after which the trap was allowed to warm up and the pressure of carbon dioxide allowed to reach the desired value. A similar procedure was used to introduce carbon tetrachloride except that the trap was cooled in a dry ice – acetone mixture.

The third system (Fig. 3) was much more elaborate and combined the second apparatus with a modification of the first to permit accurate control of the flow of gases and the use of either air or nitrogen carrier, either dry or humi-

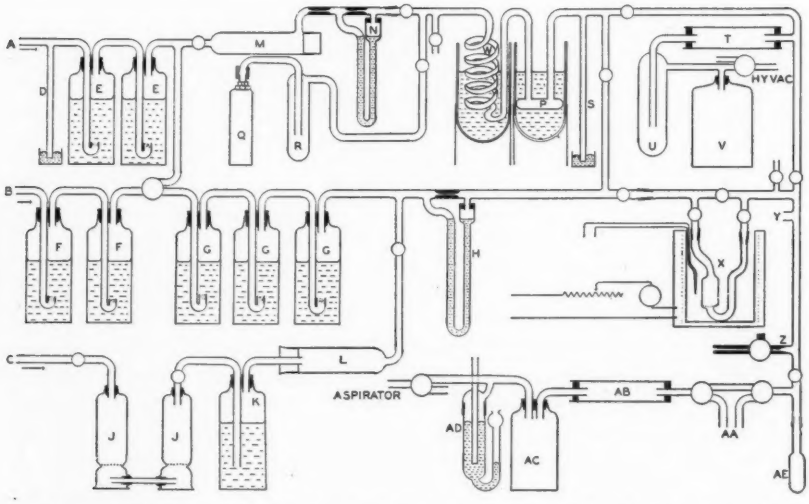

FIG. 3. *Flow system designed to study the decomposition of nickel carbonyl on the surface of charcoals and under various conditions.*

dified to any desired degree. The reaction could be carried out at various temperatures following which the charcoal bed in a small cell could be heated to various temperatures to desorb gases and decompose deposits in the charcoal. A modified Haldane gas analysis apparatus was built into the system through a Toepler pump and sampling assembly so that the gases could be collected and analyzed. Also, the tumbler was replaced by a chamber in the shape of a U so that it could be cooled by dry ice – acetone mixtures or thermostatically controlled at various temperatures with baths or furnaces. A brass screen cell could be placed in this chamber to hold the charcoal.

The X-ray tube was a Hilger all-steel Shearer tube connected directly to an all-steel mercury diffusion pump backed by a Hyvac. A copper target was used in the tube. The radiation escaped through aluminum foil windows and nickel foil, the latter to remove 'beta' radiation. A simple powder camera was used (1).

Experimental

Decomposition of Nickel Carbonyl in an Air Stream over Charcoal

Standard Chemical Company activated, unimpregnated, coconut, respirator charcoal was tumbled slowly in a dry air atmosphere containing about 1% nickel carbonyl and at atmospheric pressure and room temperature. The charcoal increased in weight slowly during a period of several hours with the products of decomposition of the nickel carbonyl. The test bulbs indicated the passage of carbon monoxide. Drying a sample of the charcoal periodically indicated that the water content was diminishing. Analysis for nickel and the weight of the deposit gave the data in Table I.

TABLE I

DECOMPOSITION OF NICKEL CARBONYL BY RESPIRATOR CHARCOAL

Sample	Charcoal, %	Water, %	Deposit, %	Nickel, %	Ratio of wt. deposit to wt. nickel
Initial	94.5	5.5			
1	84.2	4.2	11.6	6.69	1.74
2	80.6	3.7	15.7	8.16	1.92
3	67.9	2.3	29.8	13.5	2.21

It is evident that the charcoal was losing free water, and was gaining a compound containing about 50% nickel. The percentage of nickel in the deposit diminished with time. Neither Sample 2 nor 3 of Table I showed an X-ray diffraction pattern differing from that of the original charcoal. The surface of the charcoal had, however, lost its ability to decompose nickel carbonyl, since, as the charcoal approached saturation with the decomposition products of nickel carbonyl, the test bulbs indicated passage of nickel carbonyl. The charcoal had lost, also, its ability to adsorb carbon tetrachloride, the adsorption of the latter being reduced to 4 ml. of vapor (N.T.P.) per gram of charcoal from the initial 74 ml.

Decomposition of Nickel Carbonyl on Glass Surfaces

Explosions in the carburetor and connecting tubing started active centers of decomposition of nickel carbonyl which built up appreciable masses of products. One such deposit contained 61.5% nickel and some iron, and failed to yield an X-ray diffraction pattern. A second deposit contained 63.0% nickel and some iron. The X-ray diffraction pattern indicated the presence of some very finely divided nickel oxide. A third sample that was removed from the cushioning bulb connected to the apparatus and that was comparatively rich in nickel carbonyl vapor contained 85% nickel. The X-ray pattern indicated finely divided nickel and nickel oxide. The first two deposits and the third after being freed of adsorbed nickel carbonyl were stable at room temperature and drying oven temperatures (110° C.).

Adsorption of Nickel Carbonyl on Charcoal in the Absence of Air

Using the static adsorption apparatus the amount of nickel carbonyl adsorbed at various pressures of the vapor at room temperature was determined, as was also the adsorption of carbon monoxide, oxygen, carbon dioxide, and carbon tetrachloride. The data were repeated with a sample similar to No. 3 (Table I). The results are shown in Table II.

TABLE II

ADSORPTION ON RESPIRATOR CHARCOALS WITHOUT AND WITH NICKEL DEPOSIT

Vapor	Pressure, mm.	Fresh charcoal sample, ml./gm.	Nickel impregnated charcoal, ml./gm.
Carbon monoxide	363	1.6	1.1
Oxygen	331	0.0	0.8
Carbon dioxide	342	30	17.8
Nickel carbonyl	323	74	6.5–10
Carbon tetrachloride	77	90	1.3–4.0

A copper impregnated charcoal behaved similarly to the fresh charcoal sample above. In none of the cases was the nickel carbonyl decomposed, so that it is concluded that nonspecific adsorption of nickel carbonyl had taken place. Partial desorption may be accomplished by reducing the pressure.

Adsorption of Nickel Carbonyl by Charcoals Exposed Previously to Other Gases

It was observed that charcoals saturated with the decomposition products of nickel carbonyl failed to adsorb further appreciable amounts of nickel carbonyl or carbon tetrachloride. Similarly, a sample of charcoal saturated with carbon tetrachloride adsorbed but 8.2 ml. of nickel carbonyl vapor per gram of charcoal at 280 mm. pressure. A sample of charcoal exposed to a considerable quantity of arsine adsorbed about half as much carbon tetrachloride or nickel carbonyl as the fresh samples, that is, 49 and 34 ml.

respectively. Similar samples exposed to phosgene gave virtually identical data, namely 46 and 33 ml. respectively, provided the sample was dry. Wet charcoal adsorbed a small volume of vapor. This suggested that water should be considered in the series of adsorbed materials also. Decomposition or desorption resulted in the liberation of an unidentified gas when nickel carbonyl was adsorbed on a phosgene treated charcoal.

Adsorption of Arsine

Arsine prepared by decomposition of calcium or of aluminum arsenide with water or with dilute sulphuric acid was passed through a bed of activated impregnated charcoal. The X-ray diffraction pattern of the resulting charcoal and arsine decomposition products indicated the probable presence of arsenic as well as its oxides. Arsine had been reported (4) to be adsorbed and desorbed without change in the absence of air. This indicates no catalytic action by the charcoal on the decomposition of either nickel carbonyl or arsine in the absence of oxygen. However, activated charcoal is required for the decomposition of arsine in the presence of air, whereas unactivated charcoal will cause the decomposition of nickel carbonyl. Except for this difference the action of the charcoal on the two substances probably can be considered the same.

Decomposition of Adsorbed Nickel Carbonyl

Adsorbed nickel carbonyl could be decomposed rapidly and smoothly by exposure to oxygen with the production of carbon monoxide, carbon dioxide, and a deposit on the charcoal. The exact composition of the deposit depended upon the experimental method. It could be produced by saturation of the charcoal with nickel carbonyl followed by oxidation, by partial saturation and oxidation repeatedly, or by continuous adsorption and oxidation. The amount of deposit on the charcoal was essentially the same, that is, about 30% in all cases, of which slightly less than half was nickel. For purposes of calculations the formula of the deposit was assumed to be amorphous $5\ NiCO_3 \cdot NiO$, since this formula represents approximately the same amount of nickel as is found experimentally and would approximate the composition to be expected from studies reported (2, 3, 6, 9, 10, 11, 12, 14, 18, 22).

When a known amount of nickel carbonyl was adsorbed on the charcoal and decomposed by a known amount of oxygen there was an increase in volume of the system. The equilibrium atmosphere resulting contained 14 to 37 vol. % carbon dioxide. Adding this amount of carbon dioxide to that assumed to be in the nickel deposit according to the above formula indicated that 1 to 1.5 volumes of carbon dioxide was liberated for each volume of carbonyl. The residual gas liberated was probably carbon monoxide. That the carbon dioxide was not produced by oxidation of the carbon monoxide in the presence of the nickel impregnated charcoal was confirmed by bringing carbon monoxide – oxygen mixtures into contact with moist and dry nickel impregnated charcoals for prolonged periods with no evidence of reaction.

Thermal Decomposition of Nickel Carbonyl on the Surface of Charcoal.

The thermal decomposition of pure nickel carbonyl is slow at room temperature but is practically complete and instantaneous at temperatures above 100° C. (2, 6, 7, 9, 16). Decomposing a known amount of nickel carbonyl adsorbed on the surface of charcoal liberated the theoretical amount of carbon monoxide. Repetition of the process produced a sample containing 16.5% nickel. The visible nickel deposit was confirmed by observing the characteristic X-ray diffraction pattern of metallic nickel.

Decomposition of Nickel Carbonate

Preparatory to a study of the constitution of the composition of the deposit on the charcoal the decomposition of nickel carbonate was investigated. It was found that when a sample of Kahlbaum green nickel carbonate was dried it lost 9% of its weight at 110° C. and lost 27% of its weight at 325° C., leaving what appeared to be nickel oxide. This quickly reverted to a yellow carbonate on standing. The vapor pressure of carbon dioxide over the original green carbonate at various temperatures varied from 6 mm. at 20° C. to 86 at 150° C.; this indicated that instability of this compound would complicate any exact kinetic study.

Absorption of Gaseous Nickel Carbonyl by Turpentine

Turpentine, although an absorber of nickel carbonyl, failed to remove completely the nickel carbonyl present to the extent of 1% in an air stream passing through four absorbing bulbs in series at a rate of 250 ml. per min. The finding of a suitable absorber for nickel carbonyl would be an essential step in a complete kinetic study of the decomposition of nickel carbonyl.

Discussion

The decomposition of nickel carbonyl proceeds rapidly on the surface of unactivated or unimpregnated respirator charcoals. The products of decomposition would appear to be carbon dioxide and monoxide and an amorphous deposit of nickel oxide – nickel carbonate. The ratio of nickel oxide to carbonate would appear to vary with the conditions of formation. This agrees with earlier reports that indicated the ease with which the oxide is converted to the carbonate.

The adsorption of nickel carbonyl on charcoal in the absence of air would seem to be nonspecific, differing in no way essentially from the adsorption of carbon tetrachloride. If one assumes that the adsorption is monomolecular then an area of 858 sq. m. per gram of charcoal is estimated. This is in close agreement with the results of Emmett (8) who, using a similar charcoal, showed that the calculated area decreased as the molecular weight of the adsorbate increased. His data were 1830 sq. m. for water and 922 for octane. The value for nickel carbonyl would be expected to be smaller. However, the result must be considered tentative since the nickel carbonyl was at a temperature slightly below its boiling point.

Further, if monomolecular adsorption is conceded then it can be understood why oxidation of this film failed to yield a sample that would show an X-ray diffraction pattern, since particles at least 10 or more molecules thick are required even for very diffuse resolvable diffraction maxima.

A kinetic study of the decomposition of nickel carbonyl on a charcoal surface would be exceedingly complicated. In addition to the variability of product it was observed that nickel carbonate had an appreciable vapor pressure at moderate temperatures and that nickel carbonyl was not removed entirely from air by absorbing bulbs containing turpentine. Further data on the homogeneous decomposition or oxidation of nickel carbonyl would be desirable.

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